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Chemistry of

INSECTICIDES AND FUNGICIDES

BY

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PREFACE

This book is the direct result of a number of requests, made to me several years ago, that I offer a graduate course dealing with the chemistry of insecticides and fungicides. These requests came from chemists and biochemists who felt that the courses then available did not stress sufficiently this rapidly growing field of chemical endeavor, and from economic entomologists and plant pathologists who were of the opinion that their attempts to control insects and plant diseases would be facilitated by a better understanding of the chemistry of those products used as insecticides and fungicides.

The course requested was organized, and has now been taught for several years. This text is the outgrowth of my lecture notes and reference compilations. In writing it, I have tried to make it as widely useful as possible: there appears to me to be a great need for a reference work to which teachers and research workers in various fields, particularly of course in economic entomology, plant pathology and horticulture, may turn for information concerning the composition, properties, and reactions of the various chemicals used to control insects and plant diseases. With this in mind I have appended to each chapter a rather extensive bibliography as source material for those who wish to pursue any particular subject further. These bibliographies are by no means complete, but in my opinion are representative of the work in the fields which they cover.

I am greatly indebted to a number of people who have by their assistance made this book possible; to all of my former students, who were helpful in correcting errors in the earlier drafts of the manuscript; to Dr. William Crocker, Dr. F. Z. Hartzell, Miss Marian E. Lapp, Dr. R. C. Roark, Messrs. Weiss and Downs and others for permission to quote from published works. Photographs were kindly furnished by Messrs. Avens and Pearce, Dr. C. M. Smith, Dr. E. P. Killip, Mr. A. W. Clyde and Dr. R. E. Culbertson. Dr. Hubert Martin and Dr. R. W. Marsh, of the Long Ashton Horticultural Research Station, Bristol, England, not only graciously gave permission to reprint certain passages from

published material, but in addition made me welcome in their laboratories. Finally, I owe much to Dr. R. A. Dutcher, head of the Department of Agricultural and Biological Chemistry at The Pennsylvania State College for his encouragement in all of this work.

DONALD E. H. FREAR

State College, Pa.
April, 1942

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CHAPTER I

INTRODUCTION

Man Versus Plant Pests. Since prehistoric times, when man first attempted to modify his environment by cultivating for his use those plants he found most suitable for his domestic needs, there has been a struggle between the farmer and those factors which operate to reduce the crops under cultivation. The earliest method of cultivation, if the term may be applied, was probably the encouragement *in situ* of wild plants which had been found useful for the production of food, clothing, or some other daily need. This undoubtedly consisted simply of clearing away the competitive vegetation and freeing the chosen plants from the natural competition to which they are always subjected.

When such encouragement was given the selected plants, other difficulties appeared. The plants, now grown larger and probably more fruitful than in their original environment, became more attractive to man, and to insects and diseases as well. This occurred not only because of the increased size and vigor of the plant, but mainly because the natural vegetation, which had formerly grown in close proximity to the cultivated plants, was now removed. For example, when ninety plants in a given area were removed in order to encourage the ten remaining, the plant pests which originally were divided among the one hundred plants were concentrated on ten. Cultivation thus had upset the *natural balance* which always exists in primitive plant communities untouched by man.

Natural Balance in Plant Communities. The foregoing example is but one way in which the equilibrium between plants and their natural enemies may be upset by cultivation. The concentration of a large number of plants of one species in a relatively small area must necessarily encourage those pests which attack this species, not only by providing a relatively large number of plants but, by reducing the area, increase the opportunity for infestation. An isolated apple tree, for example, may be quite free from codling moth because, through chance, no moth has encountered the tree; an orchard, on the other hand, is almost sure to be infested rather

heavily if not treated; first, because the chances are much greater that a codling moth will find a suitable host, and second, because, once the colony of insects has been established, it may spread with facility through the entire plantation. Consequently, if the production of crop plants is to be carried out economically, it is necessary to find some method for the control of the pests attacking them. This has been accomplished in a number of ways.

Methods of Control of Plant Pests. Several methods may be used to reduce the population of pests on cultivated plants. Some are rather obvious, and were undoubtedly practiced from the early days of agriculture; others are the results of later, more scientific investigations. Certain systems are best adapted to the control of one type of pest; for instance, although the same general control methods are used for both insect and fungus diseases, some methods are adapted to one, some to the other. Ordinarily, it may be said that a combination of several processes is usually the most effective. The methods used to control pests are enumerated below, but in this text only chemical methods of control will be considered.

1. *Mechanical.* The removal by mechanical means of the pest, either alone or together with the affected plant parts, is often a satisfactory method of insect and disease control. The old process of hand picking Colorado potato beetles from infested plants will probably be recalled by those who were reared on farms; it was a laborious procedure, but for small areas quite effective. Certain plant diseases are controlled by pruning out affected portions and burning or otherwise destroying them.

2. *Biological.* Many plant pests, particularly insects, are themselves attacked and destroyed by other organisms. If these predatory or parasitic organisms can be encouraged, it is sometimes possible to control certain species of insects.

3. *Plant Resistance.* Certain varieties of plants exhibit varying degrees of resistance to plant pests. This phenomenon has been very useful in the control of certain fungus diseases, particularly on cereals, since it is possible by selection and hybridization to enhance the desirable characteristics in the plant.

4. *Nutrition.* It has been noted for many years that the nutritional status of a plant has a direct bearing on its susceptibility to insects and diseases. It is possible that many cases of the resistance described in the last paragraph may be explained by nutri-

tional differences. The consensus of opinion seems to be that, in general, heavy applications of nitrogen predispose plants to infection by disease. There are, however, many exceptions, and it has been stated that occasionally the reverse is true.

5. *Climatic.* Climatic conditions in a locality may favor the growth of certain plants and be unfavorable to the insects and diseases which attack them, while in other localities the reverse of this situation may obtain. These conditions undoubtedly play a part in determining the degree of insect and disease infestation, but only in isolated cases is it possible to take full advantage of this control.

6. *Chemical.* The application of chemicals is the most important method used at the present time to control plant pests. A wide variety of materials is used, alone or in combination, and applications may be made by using substances in the solid, liquid, or gaseous state. The spraying of liquid suspensions or solutions is probably the most common method, although dusting with finely divided solids is also widely used. Gases are used mainly as fumigants in confined spaces.

By the proper choice of insecticide, it is possible to control nearly all insects; many fungus diseases are combated by the proper application of fungicides, although certain fungi, as well as many bacterial and virus diseases are still not successfully controlled by chemical means.

The materials used to control plant pests may be arbitrarily divided into two classes: those used against insects are called insecticides and those used to control fungi are called fungicides or anticryptogamic substances. It should be emphasized, however, that certain materials, such as lime sulfur, function both as insecticides and fungicides.

Insecticides are further classified according to their mode of action against insects. Those materials which kill by contact with the body of the insect are logically called *contact* or *eradicant* insecticides, and those which must be ingested to become effective are known as *stomach poisons* or *protective* insecticides. Each is particularly effective against certain types of insects, and an understanding of insect anatomy is necessary in order fully to appreciate the usefulness of each type of insecticide.

Insect Types. While there are many ways in which insects may be classified, for present purposes the classification is based upon

feeding habits and the insects fall into two groups: those which have biting or chewing mouth parts and hence ingest solid food; and those in which the mouth parts have been transformed into a sucking apparatus. The latter, when feeding on plant surfaces, usually insert their sucking mouth parts through the outer epidermis into the softer interior portions and thus extract the necessary food. Obviously, while stomach poisons are extremely effective against those insects which bite fragments from the exterior of the plant and swallow them, such poisons are useless against insects which feed on the interior portions of the plant. Therefore, other means must be used.

PART I

Insecticides

STOMACH POISONS

or

PROTECTIVE INSECTICIDES

CHAPTER II

THE ARSENICALS

The arsenicals are the most widely used group of stomach poisons; they are also among the earliest materials used for this purpose.

Although accurate figures are not available, it is agreed that the consumption of arsenicals is growing rapidly. The world consumption of arsenic (as As_2O_3) in 1937 has been estimated as 120,000,000 pounds, of which 50 to 60 per cent were used in the United States.

Paris Green. Like most insecticides and fungicides Paris green was adopted as a means of combating a specific pest, in this case the Colorado potato beetle (*Leptinotarsa decemlineata* Say.). This voracious insect, a native of the Rocky Mountains, where it fed upon native solanaceous plants, began to spread eastward as soon as the westward march of agriculture invaded its native habitat. The insect soon came to feed exclusively upon potatoes, and to spread with great rapidity. In 1859 it had reached a point one hundred miles to the west of Omaha, Nebraska, and by 1868 had invaded central Missouri and southern Illinois. Four years later it had reached central New York, and by 1874 it was found on the Atlantic seaboard, having covered a distance of approximately two thousand miles in fifteen years.[1]

The person who originated the idea of using Paris green against the potato beetle is not known, but it apparently was first used in the West about 1865, and in 1868 the value of the poison appears to have been fairly well known.[2] Since no satisfactory sprayers were available, the poison was at first put on the plants with brooms, a fairly common method at that time for all materials of this nature. After the demonstration of its usefulness against the Colorado potato beetle, Paris green was used against the canker worm (*Alsophila pometaria* Harr. and *Paleacrita vernata* Peck) and later against the codling moth (*Carpocapsa pomonella* L.) and between 1880 and 1900 it was probably the most commonly used insecticide, with London purple a close second.

However, the severe burning of foliage caused by the relatively large amounts of soluble arsenic usually present in the commercial product, its property of rapidly settling from suspensions, and its poor adhesive qualities have allowed lead arsenate, a superior insecticide in these respects, to supersede it. At present, Paris green is seldom used as an insecticide on crop plants. It is, nevertheless, finding considerable use as a larvacide to control mosquitoes.[3] For this purpose it is diluted with road dust, powdered charcoal, or clay, and dusted on the surface of stagnant pools of water. A mixture containing 1 per cent Paris green is applied at the rate of 1 liter to 100 square meters. It is said[4] that the aquatic flora convert the arsenic to ethylarsine, so that there is no accumulation of arsenic in the water, although cases of human poisoning from its use have been reported.

Chemistry of Paris Green. Known also as Emerald green, French green, Schweinfurter Grün, and Mitis green, Paris green is a complex compound of copper metarsenite and copper acetate. The ratio between the two compounds is usually nearly 3 : 1, but according to Avery [5] it may be as low as 2 : 1. The formula usually given for Paris green is $(CH_3COO)_2Cu \cdot 3Cu(AsO_2)_2$. Avery, as well as Abraham [6] and Wöhler,[7] found that other acids could be substituted for acetic. Complexes of copper formate-copper arsenite, and derivatives of propionic, butyric, valeric, and succinic acids have been prepared.

Avery found, as did Wöhler, that with the acids of higher molecular weights, the ratio between the metarsenite portion of the compound and the organic portion became less, so that in the butyric acid compound there were approximately two molecules of copper metarsenite to one of the copper butyrate.

Recently Dearborn [8] has repeated Avery's investigations, and concluded that Paris green and its homologues are definite compounds of copper metarsenite and the copper salt of the corresponding acid, and that the ratio of the two constituents is very close to 3 : 1 in all cases. Further work by the same author [9, 10, 11]) indicated that the higher members of the acetic acid series, lauric, palmitic, stearic, probably melissic, as well as crotonic, oleic, erucic, and linoleic acids, form homologues. It was further shown that certain vegetable and animal oils may be used to prepare similar homologues. The compounds prepared from the oils were bluish

green in color, insoluble in water, and after drying were not easily wet with water without the use of a wetting agent. The compounds may be ground to a very fine state of subdivision, producing a light, fluffy product. These homologues of Paris green have been tested in a preliminary way [12, 13] and found to have greater toxicity against the confused flour beetle (*Tribolium confusum* Duval) than lead arsenate or Paris green itself. It would appear that these homologues bear considerable promise as new insecticides, particularly because of the possible fungicidal action of the copper present.

Paris green breaks down rather readily, even in the presence of water alone, as shown by Avery and Beans [14] and Holland and Reed.[15] The latter authors consider the reaction to be hydrolysis, resulting in the formation of soluble arsenic. Carbon dioxide and ammonia also cause decomposition. As mentioned previously, the presence of relatively large amounts of soluble arsenic precludes the use of Paris green on plants which do not possess a high degree of resistance to this element.

Paris green is manufactured commercially by boiling verdigris, a basic acetate of copper, with arsenious trioxide and acetic acid.

London Purple. Shortly after the successful use of Paris green had been demonstrated, an English firm, Hemingway and Company, proposed to Dr. C. E. Bessey, then of Lincoln, Nebraska, that a purple residue from the manufacture of dyestuffs might be of insecticidal value because of its high content of arsenic.[1] After tests, it was highly recommended by many investigators, and for a number of years it was used for the same purposes and in approximately the same amounts as Paris green.

London purple, the name given to the material by Dr. Bessey, was found on long trial, however, to be of a variable composition, and hence difficult to use, since one lot contained quantities of soluble arsenic sufficient to cause foliage injury, while the next lot might be satisfactory. This was no doubt due to the fact that it was a by-product, and not primarily produced as an insecticide. Its use declined during the last decade of the century, and has been almost entirely superseded by lead arsenate and other more uniform arsenicals.

Chemistry of London Purple. The analysis of two samples of London purple has been given [16] as follows:

	SAMPLE A Per Cent	SAMPLE B Per Cent
Arsenic	43.65	55.35
Roseaniline	12.46	....
Lime	21.82	26.23
Insoluble residue	14.57	....
Iron oxide	1.16	....
Water	2.27	5.29
Sulfuric acid	....	0.22
Carbonic acid	....	0.27

It is stated by Lodeman [1] that "some samples show that fully one-half of the arsenic is in a soluble condition." It apparently was impossible to use the material as a spray without the addition of considerable quantities of lime to counteract the injurious effects of the large quantities of soluble arsenic.

Chemically, London purple is a mixture of calcium arsenite with some calcium arsenate, and, as the analyses given above show, considerable quantities of dyestuff and other extraneous material. It was obtained as a by-product from the manufacture of magenta or other dye of a similar nature.

No attempt was made to standardize the product, apparently, as may be seen from the great difference in the arsenic content of the two samples to which reference has already been made.

Two other materials appeared on the market shortly after the introduction of London purple, and were apparently derived from the same source. These were called Paris purple and English purple, and had similar characteristics to the original London purple.

White Arsenic (Arsenious Oxide). The well known poisonous properties of arsenious oxide * probably early suggested its use as an insecticide. In 1848 Gordon [17] indicated that ants may be destroyed by a mixture of arsenious oxide and sugar. The injury produced on plant foliage was so great, however, that it never was widely used as a spray. The use of lime in conjunction with arsenious oxide, apparently was first suggested by Gillette.[18] This combination was relatively safe to use, probably because in the dilutions used all of the arsenious oxide combined with the lime to form calcium arsenite later changing to the arsenate. But the

* White arsenic under the name of *Aqua tofana* was one of the favorite poisons of the Middle Ages.

use of such "homemade" calcium arsenates was never popular, possibly because in a short time the commercial product appeared on the market.

Chemistry of Arsenious Oxide. Arsenious oxide, or arsenic trioxide, As_4O_6 (usually written as As_2O_3) is known commercially as "white arsenic" or "arsenic." Three varieties of the substance exist, the amorphous, the octahedral, and the rhombic.

The three forms have different specific gravities and melting points. The octahedral form, specific gravity 3.689, is the form which is stable under ordinary conditions. When heated, this form sublimes at 125°–150° C. The material, when powdered, is not easily wetted by water, but when heated goes into solution quite readily with alkalies. Three series of arsenites exist, derived from the corresponding acids. (The acids apparently do not exist in the free state.)

Orthoarsenites,	for	example,	K_3AsO_3
Pyroarsenites,	"	"	$K_4As_2O_5$
Metarsenites,	"	"	$KAsO_2$

The metarsenites are formed when arsenious oxide reacts with alkali hydroxides, carbonates, or bicarbonates.

Arsenious oxide is a by-product of the roasting of mineral ores. During the heating process, the As_2O_3 is sublimed and collects in the flues, from which it is later collected and purified by sublimation. Formerly considered a nuisance, the arsenic produced is now an important source of revenue to the ore refiners. It is particularly important as the raw material from which all arsenicals used as insecticides are made.

Sodium Arsenite. Several compounds, known loosely as *sodium arsenite*, are used as insecticides, particularly as baits for grasshoppers and mormon crickets (*Anabrus simplex* Hald.). Chemically these materials probably consist mainly of either sodium orthoarsenite (Na_3AsO_3) or sodium metarsenite ($NaAsO_2$) or a combination of the two. Sodium arsenite on the market is usually sold in solutions containing approximately 32 per cent of arsenic trioxide and having a specific gravity of about 1.50. It is produced by dissolving arsenic trioxide in sodium hydroxide solution. Solid preparations sold as sodium arsenite for cricket baits contain approximately 82 per cent As_2O_3, and according to Hastings and

Pepper [19] are solid solutions, not a pure chemical compound. Solutions of sodium arsenite have a very marked phytocidal effect (they are widely used as weed killers) and hence are not commonly used as sprays, although very dilute solutions are said to have fungicidal value.

Calcium Arsenate. Gillette,[18] as mentioned previously, suggested the use of a "homemade" calcium arsenite as early as 1890. It was not until some time later (about 1906), however, that calcium arsenate was first used to any considerable extent. Since the arsenic content of calcium arsenate is higher than that of lead arsenate and the cost lower, it is considerably more economical to use the calcium salt than the corresponding lead derivative.

Certain undesirable features of calcium arsenate have, nevertheless, limited its general use. The most serious undesirable quality of calcium arsenate is its relative unstability. Unless applied with an excess of lime, serious injury may result from the use of calcium arsenate upon certain plants. The mechanism of this release of phytocidal substances will be discussed later.

Calcium arsenates have, on the other hand, found considerable use as dusts, since it is simple to produce the material in a form suitable for dusting, and it is widely used on certain plants less susceptible to injury. It is estimated by Roark [20] that 45,000,000 pounds of calcium arsenate were used in the United States during 1936 and, although only approximately half as much was used in 1937, exact figures are not available at the present time. Consequently, it appears that the use of calcium arsenate, in this country at least, is declining.

Chemistry of Calcium Arsenate. There are apparently a number of calcium arsenates possible chemically. Goodwin and Martin [21] indicate that there may be a continuous series of basic calcium arsenates, with no definite break corresponding to a particular compound. It was thought by earlier workers [25] that it was possible to prepare a pure acid arsenate corresponding to the theoretical composition $CaHAsO_4 \cdot 2\,H_2O$. Robinson [22] and Lovett [23] were able in 1918 to prepare a salt having the formula $CaHAsO_4 \cdot H_2O$ from calcium chloride and sodium hydrogen arsenate according to the following reaction:

$$CaCl_2 + Na_2HAsO_4 \rightarrow CaHAsO_4 + 2\,NaCl$$

When heated to 175° C., the monohydrated salt lost the water of crystallization, leaving the calcium hydrogen arsenate. Robinson's analyses of both the monohydrated and the anhydrous salts agreed extremely well with the theoretical composition of these salts. Robinson indicated that when the anhydrous acid calcium arsenate, $CaHAsO_4$, was heated to 230° C. there was a tendency to form the pyroarsenate, $Ca_2As_2O_7$.

The existence of the tricalcium salt has been reported and denied many times. Robinson suggests three reactions which theoretically may be used to produce tricalcium arsenate:

$$3\ CaHAsO_4 + 2\ NaOH \rightarrow Ca_3(AsO_4)_2 + Na_2HAsO_4 + 2H_2O$$
$$2\ H_3AsO_4 + 3\ Ca(OH)_2 \rightarrow Ca_3(AsO_4)_2 + 6\ H_2O$$
$$3\ CaCl_2 + 2\ Na_3AsO_4 \rightarrow Ca_3(AsO_4)_2 + 6\ NaCl$$

After trial, Robinson found that the last reaction gave the most uniform product and was most practical to use. The finished product contained two molecules of water of crystallization, and after drying at 175° C., gave the following analysis:

	FOUND IN SAMPLE	THEORETICAL $Ca_3(AsO_4)_2$
CaO	42.16	42.20
As_2O_5	57.73	57.80

These results are so close to the theoretical that they would appear to prove that Robinson was working with tricalcium arsenate. Goodwin and Martin (*loc. cit.*), attempting to repeat Robinson's work, had difficulty in preparing the pure tricalcium salt, finding in every case contamination with calcium carbonate. Clifford and Cameron [25] state that there is no evidence that tricalcium arsenate can be formed from aqueous solutions, nor persist in contact with them. These authors contend that two solutions would be formed, one solid, the other liquid, if $Ca_3(AsO_4)_2$ were placed in contact with water.

The same authors are of the opinion that the earlier work (which indicated that a definite compound $Ca_3(AsO_4)_2$ existed) can be explained by the fact that the liquid solution is in equilibrium with a solid solution, the arsenic-lime ratio in the liquid phase being the same as in the solid phase. This equilibrium probably lies very close to the point where the solid phase has the ratio corre-

sponding to tricalcium arsenate. This complex, when leached, will give solutions with a constant ratio of arsenic acid to lime, which misled the earlier investigators to consider the complex a definite compound. Smith and Murray [26] state that the arsenic in commercial calcium arsenate practically never exists solely as tricalcium arsenate.

In two recent papers Pearce and Norton [27] and Pearce and Avens [28] have reported phase rule studies of the calcium arsenates. These publications, which represent the most careful studies made on the subject, indicate that at 90° C. four compounds may be separated from the system CaO-As_2O_5-H_2O. These are dicalcium arsenate, $CaHAsO_4$; pentacalcium arsenate, $Ca_5H_2(AsO_4)_4$, a compound never before isolated; tricalcium arsenate, $Ca_3(AsO_4)_2$; and basic calcium arsenate, $(Ca_3(AsO_4)_2)_3 \cdot Ca(OH)_2$. At 35° C., only three of these compounds were found, the basic arsenate being absent. This last compound is now considered to make up the greater part of the so-called "safe" commercial calcium arsenates which have recently appeared on the market. The fact that this compound was present at the higher temperature is thus of considerable practical importance in the manufacture of calcium arsenate. The relationships between the various calcium arsenates at 90° C. are shown in Fig. 1 taken from the paper by Pearce and Norton.[27]

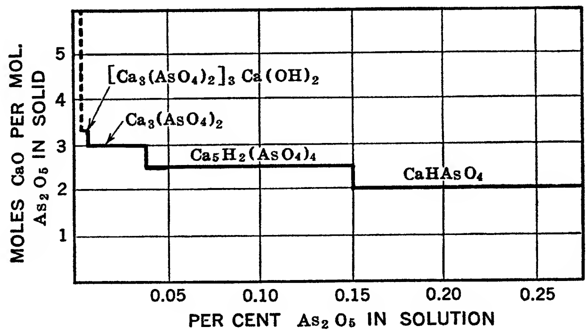

FIG. 1. Calcium arsenates formed from solutions containing various amounts of As_2O_5. (From Pearce and Norton.)

The commercial materials on the market are made from calcium oxide and arsenic oxide, and are apparently mixtures of $CaHAsO_4$, Ca_3AsO_4, $Ca(OH)_2$, $CaCO_3$ and probably other com-

pounds. As mentioned above, in some of the "safe" calcium arsenates developed recently the basic arsenate may predominate.

Reactions of Calcium Arsenate. Compared to lead arsenate, calcium arsenate is much more easily decomposed after application to the plant surfaces. According to Goodwin and Martin [21] hydrolysis of the calcium arsenate takes place in aqueous suspension and results in the formation of calcium hydroxide. This reaction (assuming the existence of acid calcium arsenate alone) may be as follows:

$$CaHAsO_4 + 2\,H_2O \rightarrow Ca(OH)_2 + H_3AsO_4$$

The reaction theoretically may go to equilibrium in the spray tank, but quite probably continues during the period after application to the plant surface and before complete evaporation of the aqueous phase. The question of just what reactions proceed during the period of drying of a spray film upon the plant surface has never been thoroughly investigated. Certainly as the aqueous phase, bearing certain substances in solution in small quantities, becomes progressively more and more concentrated, there are many possible reactions between components.

The presence of excess calcium hydroxide in the mixture apparently prevents the formation of soluble arsenic. When the calcium hydroxide is changed to the carbonate by the action of atmospheric carbon dioxide, however, soluble arsenic is liberated. This was demonstrated as long ago as 1919 by Patten and O'Meara [29] and proved conclusively by an experiment of Goodwin and Martin [21] in which varying amounts of hydrated lime were added to a suspension of dicalcium arsenate. Air was bubbled through the mixtures and samples withdrawn for analysis at intervals. The data are given in Table 1.

These authors found that carbon dioxide exerts a similar action on solid basic calcium arsenates, although at a slower rate. McDonnell, Smith, and Coad [30] reported similar results from their investigations on stored calcium arsenate. The newer, so-called "safe" commercial calcium arsenates, since they are apparently composed mainly of the basic arsenates, are thus considerably slower to react and release soluble arsenic and owe their "safeness" to this fact. The degree of safeness may be measured with considerable accuracy by the "Geneva" method of Pearce, Norton, and

TABLE 1
SOLUBLE ARSENIC IN MIXTURES OF $CaHAsO_4$ AND $Ca(OH)_2$

Composition of Original Suspension	Grams As_2O_5 per 100 cc. solution		
	After 3 days	After 11 days	After 24 days
0.113% $CaHAsO_4$	0.0625	0.062	0.058
0.113% $CaHAsO_4$+0.042% $Ca(OH)_2$	0.001	0.069	0.070
0.113% $CaHAsO_4$+0.127% $Ca(OH)_2$	0.000	0.067	0.068
0.113% $CaHAsO_4$+0.170% $Ca(OH)_2$	0.000	0.004	0.087

(Data from Goodwin and Martin [21])

Chapman.[31] This method, described in detail in Chapter XIV, consists of titrating the sample of calcium arsenate with a carbon dioxide solution to the endpoint of thymolphthalein, allowing the suspension to stand for 24 hours, and determining the soluble arsenic present. Samples of calcium arsenate containing excessive amounts of lime, which would suppress the formation of soluble arsenic, are thus placed on the same basis as samples containing no added lime, and a true value for soluble arsenic is obtained.

When mixed with other materials in a spray, the calcium arsenates apparently react with the other components to a greater or lesser extent, depending on the nature of the other materials. Marshall and Groves [32] state that larger quantities of calcium arsenate must be used to obtain the same deposit than when lead arsenate is used, because of the greater sticking ability of the latter. Their work further shows that many spreaders and stickers satisfactory for lead arsenate may be worthless or even injurious when used with calcium arsenate. A combination of calcium arsenate, zinc sulfate, and hydrated lime in the proportion 4 : 1 : 2 gave good deposit and codling moth control with low injury. The mechanism of the action of the zinc sulfate in this mixture is not understood.

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CHAPTER III

THE ARSENICALS (*Continued*)

The Lead Arsenates

Lead arsenate is the most widely used arsenical material in the field at the present time. It was estimated [1] that 44,000,000 pounds of lead arsenate were used in 1937, and unofficial estimations indicate a consumption of approximately 60,000,000 pounds in 1938.

The history of the development of lead arsenate as an insecticide is very interesting, since it probably represents the first contribution by a chemist to the field of spray materials. In 1892, F. C. Moulton, a chemist employed by the Gypsy Moth Commission in Massachusetts, first suggested the combination of lead acetate and di-sodium arsenate as an insecticide for use against the gypsy moth (*Porthetria dispar*).[2] Subsequent trials by Fernald [3] indicated that lead arsenate was far superior to the insecticides then available, and its use has increased from year to year.

As mentioned previously, lead arsenate is, from many points of view, an ideal insecticide. It is easily produced in a light, flocculent form, easily dispersible in water. After application to the plant surfaces it forms a relatively uniform deposit and exhibits a high degree of tenacity. It is not so readily decomposed as are many of the other arsenicals, and although it may cause injury to the plant, it is much less likely to do so than any of the other arsenical materials.

Against these good qualities, however, must be balanced certain undesirable features. The arsenic content per unit of weight is lower than in calcium arsenate, so that proportionately larger amounts must be used to give the same arsenic concentration; the presence of lead in the molecule increases the cost greatly over the relatively cheap calcium salt. Finally, lead arsenate is extremely toxic to all forms of life, and must be considered potentially more dangerous than calcium arsenate, because the lead as well as the arsenic is toxic and is a cumulative poison in the

animal body where it is presumably deposited in the epiphyses of the bones.

The chemistry of the various combinations between lead and arsenic has been exhaustively investigated by McDonnell and Smith.[4, 5, 6] The reader is referred to these original papers for a more complete discussion of the subject. Briefly, these authors found the following compounds possible:

NORMAL ARSENATES

Monolead Orthoarsenate—$PbH_4(AsO_4)_2$. This compound is formed by the reaction of an 86 per cent solution of H_3AsO_4 and solid $PbHAsO_4$ at about 130° C. with the addition of 2 per cent HNO_3. The concentration of arsenic acid is apparently very important for no reaction took place when 50 per cent concentration was used, and with concentrations higher than 86 per cent trilead arsenate was formed.

The monolead orthoarsenate formed by this reaction consisted of long, narrow rhomboidal plates, with a specific gravity of 4.46 15°/15°. Chemically it is very unstable, being decomposed in water solution, yielding 21.89 per cent soluble As_2O_5 in three hours at room temperature, and therefore useless as an insecticide.

Dilead Orthoarsenate—$PbHAsO_4$. This material, commonly called acid lead arsenate, is also known as bibasic lead arsenate, diplumbic hydrogen arsenate, diplumbic arsenate, and lead hydrogen arsenate. When "lead arsenate" is mentioned without further qualification, it is usually this compound which is meant.

Dilead orthoarsenate occurs in monoclinic leaflets, according to Goguel [7] and De Schulten.[8] The crystals are tabular parallel to the plane of symmetry, the latter containing the optic axes. They have an acute angle of 84°,[7,8] or 85°.[4] Extinction occurs at 21°–22° according to Goguel, and at 29° according to McDonnell and Smith. They are optically positive and the birefringence is quite high.

The specific gravity of the crystals, as given by De Schulten, is 6.076, 6.042, and 6.053, both at 15°/15° as determined by McDonnell and Smith. The amorphous material was found to have a lower specific gravity, 5.93 15°/15° [4] and 5.786.[9] Pure dilead arsenate is very sparingly soluble in water; according to

McDonnell and Smith only 0.002 gram As_2O_5 being soluble in 100 cc. of water after six hours' boiling.

Upon heating, dilead arsenate is converted into the pyroarsenate at about 280° C. and melts at a bright red heat.

Commercially, dilead orthoarsenate is prepared from arsenic pentoxide, acid, and litharge.

Trilead Orthoarsenate—$Pb_3(AsO_4)_2$. As described by McDonnell and Smith this material is light yellowish brown in color and crystalline in structure. The specific gravity is 7.32 at 15° C. This material was at one time considered to be the "neutral" or "basic" lead arsenate of commerce, but it has been shown by Robinson and Tartar [10] and Streeter and Thatcher [11] that it is in reality composed of several basic arsenates. Therefore, this compound apparently has not been used as an insecticide.

Lead Metarsenate—$Pb(AsO_3)_2$. Lead metarsenate may be produced from monolead arsenate by heating. It may also be produced from the fusion of equivalent quantities of arsenic acid and litharge (PbO), or red lead (Pb_3O_4), although the product contains some arsenites.

The crystals of lead metarsenate are hexagonal tablets with a specific gravity of 6.42. The compound is decomposed by water, so is not suitable as an insecticide.

Lead Pyroarsenates—$PbH_2As_2O_7$ and Pb_2AsO_7. These materials cannot exist in aqueous solution, and although the presence of the monolead pyroarsenate has been reported in commercial preparations by Brünnich and Smith,[12] their work has not been substantiated, and the presence of these compounds in such materials is extremely doubtful.[4]

BASIC ARSENATES

Lead Pentoxyorthoarsenate (Octalead Arsenate)—$8PbO \cdot As_2O_5 \cdot 1/2H_2O$. Strömholm [13] seems to be the first to report a compound of approximately this composition. McDonnell and Smith [6] repeated the work, and found that a compound having nearly constant composition was produced when dilead arsenate was dissolved in 10 per cent KOH, and the resulting solution poured into 5 to 8 volumes of boiling water. The compound thus prepared contained 88.31 per cent PbO, 11.28 per cent As_2O_5, 0.34 per cent

H_2O; theory for $8PbO \cdot As_2O_5 \cdot 1/2H_2O$—88.20 per cent PbO, 11.36 per cent As_2O_5, 0.44 per cent H_2O.

This compound crystallizes in thin, usually square plates, apparently belonging to the orthorhombic system. The specific gravity is 8.04 15°/15°.

Lead Hydroxy Arsenates — $Pb_4(PbOH) \cdot (AsO_4)_3 \cdot H_2O$ and $Pb_5(PbOH)_2 (AsO_4)_4$. Various formulas have been suggested for the compounds formed in this series. It is difficult to determine which of these, if any, is correct. Undoubtedly several compounds exist in commercial preparations of "basic" lead arsenate, as there appears to be a whole series of such compounds possible, their composition depending upon the concentration and proportions of the reactants used in the preparation.

Since a series rather than a single compound of this approximate composition exists, it is not practical to give physical constants. The specific gravity of the two compounds are given as 6.86 and 7.08, both at 15°/15°, respectively. The corresponding PbO/As_2O_5 ratios are 3.29 and 3.50 (approximately).

For reasons which will be discussed later, basic lead arsenate is used in certain areas in considerable quantities. One area is on the Pacific Coast of the United States, where onshore winds carry in from the ocean appreciable quantities of salt. Basic lead arsenate is also used at times as a spray on certain sensitive plants, such as peach trees.

The commercial basic lead arsenates probably approximate the composition $Pb_4(PbOH)(AsO_4)_3 \cdot H_2O$ mentioned above.

Reactions of the Lead Arsenates. Because two chemically different forms of lead arsenate are used as insecticides, it will be necessary in discussing their chemical reactions to distinguish carefully between them. Practically, the amount of acid lead arsenate used commercially is far greater than that of the basic form.

Acid Lead Arsenate. While acid lead arsenate is very slightly soluble in water, it is apparent that soluble arsenic is sometimes formed from it on plant surfaces in sufficient quantities to be injurious to the plant substratum. McDonnell and Graham [14] have shown that hydrolysis of the arsenate may take place according to the following equation:

$$5PbHAsO_4 + HOH \rightleftharpoons Pb_4(PbOH)(AsO_4)_3 + H_3AsO_4$$

These authors found that this reaction, leading to the formation of a basic compound (hydroxy mimetite), reaches equilibrium while the concentration of arsenic acid is very low but may proceed to completion if the soluble product is removed. This same basic arsenate is also formed by the action of ammonium hydroxide on dilead arsenate, as shown by Tartar and Robinson,[9] Smith,[15] and McDonnell and Smith.[4]

Headden,[16] and Haywood and McDonnell [17] have further shown that lead arsenate is decomposed by the action of dissolved salts in the water used as a suspending vehicle in the application of sprays.

The data illustrating this point are given in Table 2. These data indicate that water saturated with CO_2 exerts less solvent action on lead arsenate than pure water alone, although the difference is slight. Patten and O'Meara [18] later substantiated these conclusions.

TABLE 2

SOLUBILITY OF LEAD ARSENATE IN VARIOUS AQUEOUS SOLVENTS

Solution Composition	*Soluble As_2O_5*
Carbon dioxide free distilled water	0.45
Carbon dioxide saturated distilled water	0.32
Hard tap water as used in field spraying	4.43
CO_2-free distilled water + 0.2% NaCl	10.21
Distilled water + 0.2% Na_2CO_3	10.69

(Data from Haywood and McDonnell,[17] pp. 46–47)

According to Tucker,[19] acid lead arsenate is relatively stable between pH 2 and pH 5, and will tend to change over to other forms in contact with solutions of pH outside of this range. Tucker collected a number of samples of dew from foliage and found it had a pH between 5 and 6, which is approximately that of a saturated solution of carbon dioxide in water. He concluded that hydrolysis of the lead arsenate deposited on plant surfaces by dew and rain is not an important cause of arsenical injury, because the quantities of arsenic acid liberated in this way are relatively small.

Tucker, however, considers that the presence of small quantities of sodium chloride in the atmosphere near the coast may be sufficient to cause decomposition of the deposited lead arsenate, and this may explain the high incidence of arsenical injury in these regions.

To summarize, it appears that acid lead arsenate, unlike calcium arsenate, is not hydrolyzed in the presence of atmospheric carbon dioxide, which is ordinarily present in dews and rain. The use of hard waters containing appreciable quantities of alkali or salt may cause decomposition sufficient to produce injury on the plant to which the arsenate is applied. It would appear that the use of lime in sprays containing only lead arsenate suspended in water would increase, rather than decrease, the formation of soluble arsenic, although, as will be shown later, lime present in mixtures of lead arsenate and lime sulfur tends to decrease the injury for quite another reason.

Basic Lead Arsenate. Probably because of the limited use of this material as an insecticide, much less work on its reactions has been reported. Tucker [19] indicates that this material, "trilead arsenate," is relatively stable between pH 5 and pH 6.5, and that the lead hydroxy arsenates, $Pb_4Pb(OH)(AsO_4)_3$ and $Pb_5(PbOH)(AsO_4)_4$, were stable in the range between pH 11 and pH 6.5, below which they apparently were changed to dilead arsenate.

In general, it is considered that the basic lead arsenate of commerce is safer to use on tender foliage than the acid form, although its lower arsenic content, less desirable physical properties, and lower toxicity make it definitely inferior to the acid lead arsenate.[20]

Reactions with Other Spray Materials. Because lead arsenate is so widely used, and almost always in combination with other materials, great interest has been shown in the chemical reactions which take place between the arsenate and the other components of a mixed spray.

The use of such sprays, usually containing a fungicide in addition to the insecticide, is for obvious reasons good economy. One application, protecting simultaneously against all plant pests, is an ideal arrangement from the point of view of the orchardist, but unfortunately not all spray materials are compatible one with the other. This has been shown already in the case of calcium arsenate. Lead arsenate is compatible with more of the commonly used fungicides than the calcium salt, but it was early noticed that certain combinations increased plant injury, and studies to determine the cause and possible means of eliminating these undesirable features of the sprays have been numerous.

Lime Sulfur-Lead Arsenate Mixtures. Probably the most common fungicides used with lead arsenate in combination sprays belong to the sulfur group, particularly lime sulfur solutions. The reaction between acid lead arsenate and lime sulfur solution, when the two are mixed in the spray tank, is unmistakable: the white color of the lead arsenate is changed to brown in a matter of a few seconds, and the color becomes progressively darker with time. Apparently the first investigators to study the reaction from a chemical point of view were Bradley [21] and Tartar.[22]

These authors found that, as might be expected from our knowledge of the pH stability range, the basic arsenate reacted only slightly with the lime sulfur, while considerable decomposition of the acid form took place under the same conditions.

Ruth,[23] in an extensive investigation of the reaction taking place between these two materials, indicated that after mixing there was an increase in the concentration of thiosulfate and sulfite salts in solution. He failed to find any sulfide of arsenic and concluded that a thio-arsenate of some kind was formed.

Young [24] and others, including Robinson and Tartar,[10] noted the decided increase in soluble arsenic after mixing, and the former author found that the amount of soluble arsenic formed was in direct proportion to the amount of lead sulfide formed. He postulated a reaction between the arsenate and free hydrogen sulfide as follows:

$$2PbHAsO_4 + 2H_2S \rightarrow 2PbS + As_2O_5 + 3H_2O$$

In this case arsenic acid is undoubtedly formed from the last two compounds. Hodgkiss, Frear, and Worthley [25] found that the amount of soluble arsenic formed was proportional to the amount of hydrogen sulfide evolved.

Numerous workers have noted that the decomposition of the components of the lime sulfur-lead arsenate mixture was greater in dilute solutions, although it was found [25] that at concentrations of lime sulfur solutions greater than 1–50 the degree of decomposition appeared to be constant. Further, Wallace [26] has demonstrated that mixtures containing lead arsenate have greater fungicidal properties than similar solutions of the fungicide alone.

It would appear that when acid lead arsenate and lime sulfur solution, the latter consisting mainly of calcium polysulfides, are

mixed, the polysulfides are first broken down to yield hydrogen sulfide, which then reacts with the lead arsenate to form black lead sulfide. As by-products of these reactions, arsenic acid is probably formed from the arsenate, and this in turn combines with the calcium salts to form calcium arsenates and thioarsenates, which, as we have seen, are more or less readily decomposed. Calcium thiosulfate and calcium sulfate are probably also formed during the course of the reaction. The whole process of decomposition is difficult to follow because of the number of components, and it is impossible to represent in the conventional chemical equation. The two important facts to keep in mind are these: soluble arsenic is of importance as a cause of injury, and should be kept at as low a concentration as possible; the polysulfide sulfur, as will be shown later, is the active principle of lime sulfur solutions, and should be kept at as high a level as possible for maximum efficiency. How these aims may be accomplished is discussed later under multiple mixtures.

Calcium Hydroxide-Lead Arsenate Mixtures. Pickering,[27] Lovett,[28] and others have indicated that the addition of calcium hydroxide to acid lead arsenate reduced the amount of soluble arsenic in solution. This was explained by Robinson [29] and Campbell [30] as being due to the formation of calcium arsenate and arsenate of lead of a more basic nature. Mogendorff,[31] however, was of the opinion that the lead salt is converted into basic lead arsenate and a very insoluble basic calcium arsenate, the latter compound breaking down in the presence of carbon dioxide to form a less basic compound, and then to tricalcium arsenate. This compound may, in this author's opinion, cause arsenical injury.

Van der Meulen and Van Leeuwen [32] and Ginsburg [33] concluded that soluble arsenic as such is not free to act upon the plant until all of the lime becomes carbonated. The actual sequence of events would appear, then, to be this: acid lead arsenate, in the presence of calcium hydroxide, is slowly acted upon by the latter, forming a calcium arsenate and probably a lead hydroxide. The calcium arsenate is relatively stable in the presence of an excess of calcium hydroxide, but as soon as the hydroxide becomes completely carbonated through the action of atmospheric carbon dioxide, soluble arsenic is liberated.

Multiple Mixtures—Correctives. Various combinations of lead arsenate and two or more other ingredients have been suggested from time to time. Some of these combinations have aimed at more complete control of plant pests under specific conditions, such as the control of both chewing and sucking insects as well as fungi by a combination of the arsenate with a contact insecticide and a fungicide. Little work has been reported on the chemical reactions taking place in such mixtures.

By far the greater number of multiple mixtures containing lead arsenate have one of two aims: (1) to decrease the injury of the mixture to the plant through the addition of correctives, as in the case of lime added to lead arsenate-lime sulfur combination, or (2) the increase in the efficiency of the mixture through the use of wetting, spreading, or sticking agents. Such agents have been called *adjuvants*, and a discussion of such materials and their combinations will be presented later.

Correctives for lead arsenate-lime sulfur combination sprays are many. Robinson [29] was apparently the first to suggest that lime, when added to the mixture, reduced the amount of soluble arsenic set free, and preserved the polysulfide content of the fungicide. Robinson's explanation of the action was expressed in the following reaction:

$$3PbHAsO_4 + Ca(OH)_2 \rightarrow Pb_3(AsO_4)_2 + CaHAsO_4 + 2H_2O$$

Mogendorff [31] disagreed with this conclusion, stating that the basic arsenate of calcium is formed rather than the acid form. Swingle,[34] studying dusting mixtures of sulfur, lime, and acid lead arsenate, suggests that these reactions take place:

$$3Ca(OH)_2 + 3S \rightarrow CaS + CaSO_3 + 3H_2O$$
$$CaS + PbHAsO_4 \rightarrow CaHAsO_4 + PbS,$$

while a portion of the calcium arsenate formed comes from the direct reaction:

$$PbHAsO_4 + Ca(OH)_2 \rightarrow Pb(OH)_2 + CaHAsO_4$$
$$PbHAsO_4 + CaCO_3 \rightarrow PbCO_3 + CaHAsO_4$$

Hodgkiss, Frear, and Worthley [25] found that when one pound of slaked lime was added to 100 gallons of a mixture composed of

lead arsenate and lime sulfur, soluble arsenic, as As_2O_5, was decreased from 12.10 grams to 6.40 grams per 100 gallons, both mixtures being composed of 1 to 50 liquid lime sulfur and 3 pounds of lead arsenate per 100 gallons. As the quantity of lime in the mixture was increased, a decrease in the soluble arsenic was found, until at the highest amount used, 9 pounds per 100 gallons, only 3.20 grams of As_2O_5 were found to be soluble. A significant finding in these studies was the fact that, in the mixtures containing lime, detectable quantities of free hydrogen sulfide were never found. The addition of lime, however, failed to retain the sulfide sulfur in solution at as high a level as in a corresponding solution of lime sulfur alone. This work confirms the earlier findings of Goodwin and Martin.[35]

Proteinaceous materials have been suggested as correctives by many workers, possibly more from the standpoint of their effect on the spreading, wetting, and adhesive properties of the spray solution than for their effect on the chemical composition of the solution. Vermorel and Dantony [36] as early as 1912 suggested the use of gelatin and casein to increase the wetting power of sprays. Such materials, however, do affect the chemical reactions taking place in the spray mixture, and Goodwin and Martin,[35] and Hodgkiss, Frear, and Worthley [25] have found that the addition of casein or dried milk powder caused an increase in the amount of soluble arsenic formed in lime sulfur-lead arsenate spray mixtures. This increase was apparently proportional to the amount of milk powder added,[25] and has been explained by Thatcher and Streeter [37] as being due to the protein material. It should be pointed out in this connection that the use of casein materials does decrease the extent of the decomposition of the polysulfides present, and hence serves a useful purpose. Hodgkiss, Frear, and Worthley [25] have shown that combinations of lead arsenate, lime sulfur solution, lime and skimmed milk powder gave lower amounts of soluble arsenic and at the same time higher amounts of polysulfide sulfur than triple mixtures. The most desirable spray mixture was obtained when equal quantities of lime and milk powder were used.

The use of gelatin in combination with lead arsenate and lime sulfur, according to Goodwin and Martin,[35] increases the formation of soluble arsenic, but has no effect on the reaction of the calcium

sulfide, and in general retards the decomposition of the mixed spray.

Andrew and Garman,[38] and Thatcher and Streeter[37] have noted that the addition of nicotine sulfate apparently had little effect on the composition of a mixed lead arsenate-lime sulfur spray. The former authors found that the order of mixing of the ingredients had considerable effect on the composition of the resulting mixture. It should be added parenthetically here that the procedure usually followed is to dilute the lime sulfur nearly to its final volume in the spray tank, then to add the lead arsenate mixed with a small volume of water just before application.

Manganese sulfate and ferrous sulfate have been used as correctives in combination arsenate-lime sulfur sprays, as well as various other metallic salts, such as zinc oxide, ferric oxide, and aluminum oxide. Apparently the metallic oxides were first suggested as correctives by Ginsburg,[39] who found that zinc oxide was the best corrective from the point of view of elimination of soluble arsenic, but that the zinc oxide itself was toxic to apple and peach foliage. Ferric oxide, harmless in itself in the concentrations used, prevented arsenical injury to apple foliage, but did not entirely eliminate the injury to peach foliage. However, the use of ferric oxide caused considerably greater retention of the lead arsenate deposit, indicating that it was of value as an adhesive.

Zinc sulfate, proposed by Roberts and Pierce[40] as a corrective for arsenate sprays on peaches, has proved to be extremely useful and is in quite general use. Ferrous sulfate, used as early as 1911 by Volck[41] as a corrective for lime sulfur, has been found by Kearns, Marsh, and Martin[42] to reduce arsenical injury as well.

Manganese sulfate has come into use within the past few years as a corrective, and as little chemical work has been done on the subject, it is to be supposed that it behaves in much the same way as ferrous sulfate.

The mode of action of these metallic salts as correctives is not well understood, even though it is believed by some that they act to produce elemental sulfur from the polysulfides present in lime sulfur, and hence prevent the interaction between these polysulfides (or their decomposition product, hydrogen sulfide) and lead arsenate. In effect, then, these correctives may produce a form of wettable sulfur in the spray tank from the lime sulfur.

Miscellaneous Arsenical Materials. Manganese arsenates have been prepared and have found some use as insecticides, although they were found by Dearborn [43] and others to be less effective than lead arsenate. Zinc arsenite, suggested first by Luther,[44] has found some application on the Pacific coast, but has not been used extensively elsewhere because of its toxic action on plants. Schoene [45] has shown that, although the material is low in soluble arsenic, the action of carbon dioxide produced considerable quantities of soluble arsenic under field conditions.

Basic copper arsenate, $Cu(CuOHAsO_4)$, has recently been proposed as an insecticide by Witman, Waters, and Almy.[46] According to these authors, this material is a very stable crystalline substance containing 56.2 per cent copper oxide (44.8 per cent metallic copper) and 40.6 per cent arsenic pentoxide, and 3.2 per cent water of constitution. It is not hydrolyzed by water, and only reacts slightly with carbon dioxide. These authors found it to be compatible with lime, calcium caseinate, and blood albumin. Sodium chloride has no effect on its solubility, but it reacts slowly with liquid lime sulfur. Waters, Witman, and De Long [47] have shown that basic copper arsenate is as toxic as lead arsenate when used against a variety of insects. Further work is necessary before this material can be properly evaluated, but the presence of copper in the molecule should make it valuable as a fungicide as well as an insecticide.

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CHAPTER IV

FLUORINE COMPOUNDS AND MISCELLANEOUS NON-ARSENICALS

Compounds of fluorine have long been used as insecticides, particularly against household insects. Within the past twenty years, considerable work has been done on various compounds of this element as insecticides against field crop pests as well, and a voluminous literature has resulted. Carter and Busbey [1] have prepared a very complete bibliography of the various papers on fluorine and list nearly 700 titles.

Fluorine occurs in many compounds, widely distributed. The element combines readily not only with most of the metals, but with many nonmetals, forming complex compounds, such as the fluosilicates, fluoborates, fluoaluminates, fluotitanates, and many others. In addition, fluorine acts similarly to the other halogens in forming substituted organic derivatives.

In general, the more soluble compounds of fluorine, both organic and inorganic, have been used as mothproofing agents, household insecticides and fly poisons, for wood preservation and poison baits, while the insoluble materials have been used on field crops. The compounds of fluorine are highly toxic to all forms of life, and should be used with great caution. For a review of the physiological effects of the element, see McClure.[2]

Fluorides

Sodium Fluoride—NaF. This compound was probably the first of the fluorine compounds used against insects. As early as 1896 a British patent was issued to Higbee [3] for "improved composition of material for destroying insects." Under this patent several fluorides and fluosilicates and borofluosilicates were suggested. Its solubility in water prohibits its use in field sprays, but it is effective as a dust against cockroaches and other household insects, and is a common constituent in roach and insect powders. Shafer [4] found that roaches walking through powdered

sodium fluoride pick up the powder on the exudations of the body. From here it may be absorbed through the integuments, or be ingested by the insect during the process of cleaning itself. Phelps [5] tested sodium fluoride as a muscicide, and found it effective, but because of its poisonous nature, rather dangerous to use. Snyder [6] found that a 2 per cent solution of sodium fluoride protected wood pulp products against termites. The compound is also commonly used to control lice, particularly on poultry and domestic animals, silverfish (*Lepisma* sp.), ants and mites. Because of its high toxicity it has been used in baits and traps to catch insects, in conjunction with suitable attractants. According to Roark,[7] 4,000,000 pounds of sodium fluoride were used in the United States during 1936.

Sodium fluoride is manufactured commercially from hydrofluoric acid, which is made by treating fluorspar or other nonsiliceous fluoride with sulfuric or other nonvolatile acid. Some hydrofluoric acid is produced as a by-product in the production of phosphate fertilizer. Another method for the production of sodium fluoride is the reaction between sodium carbonate and a silicofluoride according to the reaction:

$$Na_2SiF_6 + Na_2CO_3 + H_2O \rightarrow 6NaF + H_2SiO_3 + 2CO_2$$

(U. S. patent 1,382,165).

Other Fluorides. In addition to ferric fluoride, FeF_3, mentioned by Higbee,[3] other fluorides have been suggested as insecticides or for related purposes. These include: zinc fluoride, ZnF_2, suggested as a wood preservative by Nowotony [8] in 1923; barium fluoride, BaF_2, suggested by Gasow [9] as an effective dust against the pine moth (*Bupalus piniarius* L.); calcium fluorspar, magnesium, strontium, copper, barium, and lead fluorides tested by Marcovitch [10] against mosquito larvae (*Culex quinquefasciatus*). The last author reports that at concentrations of 1–100 these salts required the following time (in hours) to produce 50 per cent mortality in the larvae: calcium fluoride, 84; magnesium fluoride, 54; strontium fluoride, 55; copper fluoride, 6; barium fluoride, 3; and lead fluoride, 1.5. Potassium fluoride has been used as a wood preservative, and aluminum fluoride is mentioned by Dyson [11] as a substitute for lead arsenate.

The most soluble simple metallic fluorides other than sodium fluoride have not found any wide use as insecticides, apparently on account of the severe burning on plants, although their use as wood preservatives seems to be growing in popularity.

THE FLUOSILICATES (Silicofluorides)

Higbee's patent, mentioned in the previous section, covered the use of sodium and ferric fluosilicates as insecticides. This appears to be the first mention in the literature of this use for these materials. A number of the fluosilicates have since been tried as insecticides, and these will be discussed below.

Sodium and Potassium Fluosilicates—Na_2SiF_6 ($2NaF \cdot SiF_4$); K_2SiF_6. Sodium fluosilicate was early used in insect powders as a substitute for sodium fluoride, and Marcovitch [12] found it to be effective against chewing insects, particularly against the Mexican bean beetle (*Epilachna corrupta*).[13] Subsequent work indicated that this substance under certain conditions caused considerable injury to plants. Attempts to correct this with lime were not wholly successful. According to Roark,[14] alkalies such as sodium carbonate, frequently present in commercial sodium fluosilicate as an impurity or in certain waters used as diluents in spraying, react with the fluosilicate to produce sodium fluoride, according to the reaction:

$$Na_2SiF_6 + 2Na_2CO_3 + H_2O \rightarrow 6NaF + H_2SiO_3 + 2CO_2$$

The sodium fluoride formed, as has been shown, is relatively soluble and may easily be present in large enough quantities to become toxic to the plants. Calcium and magnesium salts react with sodium fluosilicate to form first calcium or magnesium fluosilicate, and in turn the corresponding fluoride. Roark further points out the possibility of alkaline plant excretions entering into the decomposition reactions. Marcovitch [15] showed that sodium fluosilicate was eight times as toxic to mosquito larvae as sodium fluoride but in spite of its high toxicity and relatively low cost, the danger of possible phytocidal action has discouraged its wide use as a spray or dust. Sodium aluminum fluosilicate (0.52 per cent solution) is sold for mothproofing clothing, furniture, etc. Sodium silicofluoride is widely used, moreover, as a mothproofing

agent, particularly since it has been found by Minaeff and Wright [16] that wool possesses a great affinity for the fluosilicates and, therefore, these materials may be applied as dilute solutions.

Potassium fluosilicate, as tested by Snapp and Thomson,[17] was found to be effective against plum curculio, but its relatively high price has apparently prohibited its general use. It appears to be very similar in reactions and general behavior to the sodium salt.

Sodium fluosilicate is a relatively dense material, the commercial forms, according to Marcovitch,[18] having a volume of 30 cubic inches to the pound. To increase the bulk of the substance for dusting purposes, a "light" and "extra light" sodium fluosilicate were marketed at one time. These contained from 70 to 75 per cent sodium fluosilicate, the balance being alumina. Ordinary sodium fluosilicate is made from hydrofluosilicic acid and soda ash according to the following reactions:

$$CaF_2 \text{ (fluorspar)} + H_2SO_4 \rightarrow 2HF + CaSO_4$$
$$6HF + SiO_2 \text{ (sand)} \rightarrow H_2SiF_6 + 2H_2O$$
$$H_2SiF_6 + Na_2CO_3 \text{ (soda ash)} \rightarrow Na_2SiF_6 + H_2O + CO_2$$

Calcium and Magnesium Fluosilicates—$CaSiF_6 \cdot 2H_2O$; $MgSiF_6 \cdot 6H_2O$. Marcovitch [13] apparently was the first to use these salts as insecticides. He found them both to have satisfactory toxicity against chewing insects. Calcium fluosilicate has been further tested by many workers and found to be effective against the Mexican bean beetle,[19] European corn borer,[20] the strawberry weevil,[21] and other insects. Carter [22] has pointed out that material sold as "calcium fluosilicate compound" and termed by many entomologists as "calcium fluosilicate" is in reality a complex by-product of the phosphate fertilizer industry, and may contain considerable extraneous material. He gives the analysis of a commercial sample as: calcium, 16.4 per cent; fluorine, 11.4 per cent; total water-soluble fluorine, 9.8 per cent; phosphorus pentoxide, 27.3 per cent; iron and aluminum oxides (as Fe_2O_3), 18.2 per cent.

Magnesium fluosilicate has not been so widely tested, but has been used as a wood preservative, apparently with some success. Magnesium fluosilicate is readily soluble in water (64.2 parts per

100 in cold water); hence it probably would be most useful in applications of this kind.

During recent years little work has been done on these particular fluosilicates, apparently because of the demonstrated superiority of the barium salt and of cryolite.

Barium Fluosilicate—$BaSiF_6$. This relatively insoluble salt (0.030 part per 100 in water at 21.0° C.) [23] was first used as an insecticide about 1926 [24] against the Japanese beetle. Its low solubility and relatively high toxicity have led to its rapid adoption. Marcovitch [25] found barium fluosilicate more toxic to adult insects than cryolite. More work has been reported on the insecticidal value of this salt than any other of the fluosilicates, and with cryolite it enjoys the best reputation. Foliage injury is usually not severe, and the toxicity to insects is relatively high. The great disadvantage to the material is its cost, which is higher than that of natural cryolite.

Like many other fluorine compounds, barium fluosilicate is not compatible with nicotine, calcium arsenate,[26] Bordeaux mixture, soap solutions, or lime sulfur.[27] When used in a dust mixture, common diluent materials are talc, charcoal, clay, and flour. A mixture of barium fluosilicate and sodium fluoaluminate is marketed as an insecticide.

Miscellaneous Fluosilicates. Fluosilicates of metals other than those previously mentioned have been suggested as insecticides, but none has gained wide acceptance. Among those mentioned are cadmium, aluminum, and copper, found by Fleming [27] to have little effect on the Japanese beetle; strontium and zinc fluosilicates, found by the same author to be moderately effective against this insect. The double salt, zinc magnesium fluosilicate, was found by Barrett to be extremely damaging to walnut trees when used as a dust.[28] Carter [23] has summarized the data available on the solubilities of the fluosilicates, and it appears that the salts of the heavy metals are all relatively soluble in water.

Organic fluosilicates, such as those of di-n-butylamine, pyridine, piperidine, and 6-ethoxy-2-amino-benzothiazole have been patented (British 396,064, 1933) as insecticides, and this same patent covers the use of an aqueous solution of di-n-butylamine fluosilicate or quinoline fluosilicate as mothproofing agents for wool, fur, and the like.

A number of double fluorides of aluminum with the alkali metals are found as naturally occurring minerals, such as cryolite ($AlF_3 \cdot 3NaF$), cryolithionite ($2AlF_3 \cdot 3NaF \cdot 3LiF$), chiolite ($3AlF_3 \cdot 5NaF$), ralstonite ($2NaF \cdot MgF_2 \cdot 6AlF_3(OH)_3 \cdot 4H_2O$) and pachnolite ($AlF_3 \cdot CaF_2 \cdot NaF \cdot H_2O$). Other double salts have been prepared, but from the point of view of their possible insecticidal use, cryolite is probably the most important.

THE FLUOALUMINATES

Sodium Fluoaluminate—(sodium aluminum fluoride; cryolite), Na_3AlF_6 or $AlF_3 \cdot 3NaF$. Occurring in Greenland as cryolite, sodium fluoaluminate has long been used in the manufacture of aluminum. According to an analysis quoted by Marcovitch and Stanley,[29] the natural mineral contains approximately 98 per cent of pure sodium fluoaluminate, with small quantities of silica; sodium sulfate, iron oxide, and moisture as impurities. Occurring as monoclinic crystals, natural cryolite when ground forms a heavy powder not well suited to insecticidal use. Synthetic cryolite, on the other hand, is a light amorphous powder, better adapted to use in dusting mixtures or suspended in water. The synthetic form is soluble only to the extent of one gram in 1,639 cc. of water [29] and a water suspension has a pH of 6.2.

Synthetic cryolite may be made by the Howard process (U. S. Patent 1,475,155) from aluminum fluoride, ammonium fluoride, and sodium chloride according to the reaction:

$$AlF_3 + 3NH_4F + 3NaCl \rightarrow Na_3AlF_6 + 3NH_4Cl$$

Marcovitch [29] first used cryolite as an insecticide in 1929. Its use was a logical extension of the earlier work done by him on other fluorine compounds. He found cryolite to be slightly less toxic than barium fluosilicate, but both materials gave satisfactory control of the Mexican bean beetle, when used at the rate of one pound in 50 gallons of water, and against other insects when used as a dust, diluted with two parts of lime.

Earlier in this same paper, Marcovitch points out that a reaction takes place between cryolite and lime:

$$2Na_3AlF_6 + 6Ca(OH)_2 \rightarrow 3Na_2O_3 + 6CaF_2 + 6H_2O$$

forming calcium fluoride and sodium aluminate. This recalls the criticism raised by Roark [14] of the use of fluosilicates. Roark questioned the use of lime in combination with the fluosilicates, since it has been demonstrated that a reaction, resulting in the formation of calcium fluoride, took place, and pointed out that a more economical procedure would be to use the fluoride directly. It would appear that the same argument would hold in the case of cryolite; if calcium fluoride is formed when cryolite is applied with lime, it would seem to be equally satisfactory to apply calcium fluoride directly.

Following its introduction, cryolite, both natural and synthetic, soon was widely used against a variety of insects on many plants. In general, both forms of cryolite have been found to be efficient insecticides, and usually produce little plant injury, although on certain plants, notably the peach, injury may be serious.[30]

Cryolite is compatible with a greater variety of materials than many of the other fluorine containing insecticides; it has been successfully used with mineral and fish oils, soaps, and flotation sulfur. It is decomposed by alkalies, so it is presumed that decomposition would take place if mixed with lime sulfur or Bordeaux mixture.

Miscellaneous Fluoaluminates. Carter [31] discusses the preparation of the potassium, lithium, and ammonium fluoaluminates, and describes their physical properties. These materials were never widely used as insecticides, however, and little is known of their properties in this respect. Organic fluoaluminates, as well as organic salts of fluorine in combination with titanium and tin, have been patented as insecticides [British patent 332,227 (1930)] but have not been developed commercially.

MISCELLANEOUS INORGANIC STOMACH POISONS

A wide variety of materials have at one time or another been suggested as protective insecticides. Most of these have been tried and found to be unsuited for the purpose, although a few of the newer materials have not been thoroughly tested.

Two salts of copper, cuprous cyanide, CuCN, and cuprous thiocyanate, CuCNS, have been suggested by Moore and Camp-

bell.[32] The first compound was found to be highly toxic to the Japanese beetle, the latter effective against the tent caterpillar (*Malacosoma americana*); Bulger [33] and Fleming and Baker.[34] Further trials, however, failed to show any great superiority over available materials.

Lead chromate, $PbCrO_4$, a pigment used in the paint industry, has been suggested as an insecticide, but trials by Johnson [35] on the potato beetle indicate that it was definitely inferior to the arsenicals. Phosphorus has been used as a poison for cockroaches, and tartar emetic (potassium antimonyl tartrate $KSbOC_4H_4O_6 \cdot 1/2H_2O$) is used in ant poisons and occasionally as a spray.

Borax, $Na_2B_4O_7$, formerly was used as a constituent of ant poisons, but is not widely used for this purpose at present. Barium carbonate, $BaCO_3$, has also been used as a stomach poison. Certain formulas for grasshopper baits called for the use of magnesium sulfate (Epsom salts), $MgSO_4$, although some doubt exists as to the usefulness of this compound as an insecticide.

Thallium sulfate (thallous sulfate, Tl_2SO_4) is used to some extent as an ant and rodent bait. It is prepared mainly as a by-product from the flue dusts in plants producing sulfuric acid by the oxidation of pyrites. Because it is extremely toxic to all forms of life, thallium sulfate should be used with great caution.

Organic Stomach Poisons

A great many organic compounds have been tested as insecticides, particularly in recent years, in an effort to find substitutes for the more toxic inorganic salts. Certain plant products, such as nicotine and rotenone, function to a certain extent as protective insecticides but, because they primarily act as contact poisons, they will be considered under that classification.

Hellebore. One of the earliest used plant poisons, the ground rhizome of white hellebore (*Veratrum album* Linn.), has been used successfully against insects on currants and gooseberries. White hellebore is a hardy perennial plant belonging to the family Liliaceae, found in a wild state in mountainous regions of Europe and North Asia. The rhizomes are dug in the autumn, dried, and ground for use as an insecticide. The active principles are a group of alkaloids, the best characterized of which are jervine,

$C_{26}H_{37}O_3N$; pseudojervine, $C_{29}H_{43}O_7N$; rubijervine, $C_{26}H_{43}O_2N$; protoveratridine, $C_{26}H_{45}O_8N$; and protoveratrine, $C_{32}H_{51}O_{11}N$. The constitution of these alkaloids is not known. The plant material contains from 0.5 to 1.0 per cent of total alkaloids.[36] The most recent work on the subject by Poeke[37] indicates that the molecular formulas previously found for the hellebore alkaloids may be open to question. Poeke also claims to have identified a new alkaloid, named by him "germerine," $C_{36}H_{57}O_{11}N \cdot H_2O$.

Cevadine and its salts are intensly poisonous, and protoveratridine and rubijervine, on the other hand, are reported to be non-toxic. Green hellebore (*Veratrum viride* Ait.) has sometimes been used as an insecticide as well; this contains jervine and pseudojervine mentioned previously and, in addition, cevadine, $C_{32}H_{49}O_9N$, and veratridine, $C_{37}H_{53}O_{11}N$.

Just which of these alkaloids is useful as an insecticide is not known. Hellebore is not used to any considerable extent except in unusual instances, such as on nearly mature currants, in which case the use of arsenicals would leave an objectionable residue. Hellebore powder deteriorates rapidly on exposure to air, and hence only freshly ground preparations should be used. Its effectiveness as an insecticide in the field is also lost rapidly after application.

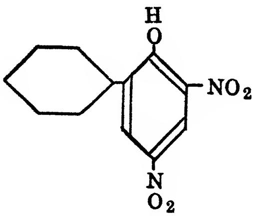
The hellebore used as an insecticide should be carefully distinguished from a drug known by the same name derived from *Helleborus niger* Linn. and *H. viridis* Linn. This does not have insecticidal properties.

SYNTHETIC ORGANIC COMPOUNDS

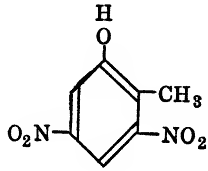
Dinitro Derivatives. A large number of organic compounds have been suggested as stomach insecticides. One of the first so used was dinitro-o-cresol. This compound and its alkali salts were investigated by Tattersfield, Gimingham, and Morris[38] and it was determined that, although the material was highly toxic to insects, it caused severe foliage injury. Recently Smith, Siegler, and Munger[39] investigated a series of organic compounds as insecticides against codling moth larvae. They found that 3,5-dinitro-o-cresol and p-iodonitrobenze were both highly toxic to this insect, and found further that replacing the phenolic hydrogen in the molecule with an acetyl or methyl group gave high toxicity.

They found no relationship between chemical constitution and toxicity.

Kagy,[40] in a study of the calcium, magnesium, lead, and copper salts of dinitro-o-cyclohexylphenol (2,4-dinitro-6-cyclohexylphenol), found the calcium salt to be most toxic. Boyce, Kagy and Hansen [41] have further investigated the possibilities of this compound. Dinitro-cresol is used at present as an ovicide in



2,4-dinitro-6-cyclohexylphenol



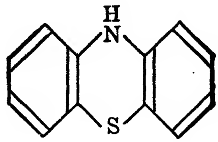
3,5-dinitro-o-cresol

dormant sprays: it remains to be seen if a derivative of insecticidal value which will be non-toxic to plants can be produced.

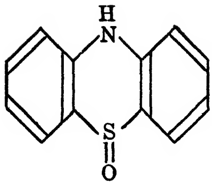
Campbell, Sullivan, Smith, and Haller [42] in 1934 found that of a number of sulfur-containing organic compounds tested against mosquito larvae, the most toxic was thiodiphenylamine (phenothiazine), $C_{12}H_9NS$. This substance was more toxic than rotenone, and was effective against the larvae used at dilutions as low as 1 : 1,000,000. This work was confirmed by King.[43] Knipling [44] found phenothiazine to be non-toxic to higher animals, and the compound has been extensively investigated by De Eds and associates.[45, 46]

Phenothiazine. Phenothiazine, according to Bernthsen,[47] is a light yellow crystalline substance, insoluble in chloroform and slightly soluble in water. It is not easily oxidized in air, turning slightly greenish, probably due to the formation of thionol. Further oxidation results in the formation of a red compound, probably phenothiazone. Other oxidation products associated with the decomposition are phenothiazine sulfoxide, leucophenthiazone, phenthiazone, leucohydroxy-phenthiazine, and hydroxyphenthiazone. The last four compounds were called oxythiodiphenylamine, oxythiodiphenylimid, dioxythiodiphenylamine, and dioxythiodiphenylimide, respectively, by Bernthsen.[47] The structural for-

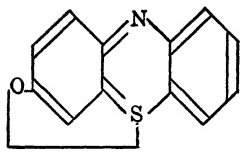
mulas for these compounds are as follows:



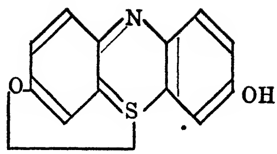
Phenothiazine



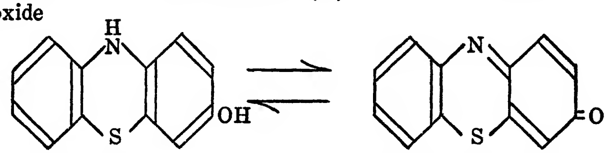
Phenothiazine Sulfoxide



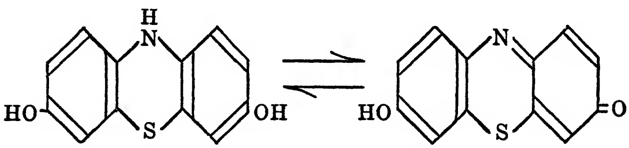
Phenothiazone (a)



Thionol



Leuco-phenthiazone   Phenthiazone (b)



Leuco-hydroxy-phenthiazone   Hydroxyphenthiazone

The nomenclature of these compounds has not been definitely established; in older works, phenothiazine is referred to as phenthiazine, and apparently phenothiazone and phenthiazone are synonymous, although Gersdorff and Claborn [48] show it as containing an oxygen ring (*a*), while De Eds and Eddy [45] give formula (*b*) without the ring structure.

Phenothiazone and phenothiazine sulfoxide were found [48] to be only slightly toxic, if at all, to codling moth larvae. Gersdorff and Claborn [48] found phenothiazone, however, to be the most

toxic of the materials of this group tested against goldfish, it being ten times as toxic as phenothiazine. These workers further found that phenothiazine sulfoxide and thionol were not toxic to the goldfish used. On exposure to the air, solutions of phenothiazine took on a reddish color, and a similar change took place in solutions of phenothiazine sulfoxide. This change in color was apparently due to the formation of phenothiazone.

Smith [49] found that samples of phenothiazine could be divided, by extraction with ether, into two fractions. The ether soluble portion, which was deep red in color, was toxic to insects; the insoluble fraction non-toxic. The work of Goldsworthy and Green [50] indicated that, as a fungicide, phenothiazone was highly potent, while the unoxidized phenothiazine was not.

From this work, it appears that phenothiazine, when applied to the plant in the form of a spray, is oxidized to phenothiazone, a more toxic substance. Further work should establish whether or not phenothiazine is an efficient insecticide for field use. Phenothiazine is used to some extent as an anthelmintic.

Miscellaneous Organic Compounds. Many other organic compounds have been found in laboratory tests to have insecticidal value. Guy,[51] for example, reports testing approximately one thousand such compounds. While many did not show any promise as insecticides, he lists the following classes of compounds, members of which may be potential insecticides:

Chromium salts—piperidinum tetrathiocyanato diamino chromium was the most toxic coordinated compound tested. Decomposition of the material took place, however, when used in the field.

Thiazines—thiodiphenylamine (phenothiazine), discussed previously, appeared to be the most promising compound in this group.

Thiuram sulfides—compounds of this group act as repellents, and tetramethylthiuram monosulfides and tetramethylthiuram disulfide were particularly effective.

Thiocarbamates—certain members of this group also acted as repellents, although not so effectively as the best of the thiuram sulfides.

Questal et al [52] tested a large number of synthetic organic compounds as stomach poisons, using the larvae of the European

corn borer (*Pyrausta nubilalis* Hubn.) as test insects. The following compounds gave the highest mortality: p-Bromoazobenzene, p-iodoazobenzene, o-iodonitrobenzene, p-iodonitrobenzene, phenazine, phenazine oxide, p-bromohydroazobenzene, azoxybenzene, 4,6-dinitro-o-cresol, 1-nitronaphthalene, and fluorene. Swingle et al [53] found phthalonitrile (orthodicyanobenzene) to have a relatively high toxicity to several species of insects, although under field conditions the toxicity was lost rather rapidly. Phillips et al [54] have reported that p-aminoazobenzene hydrochloride was highly toxic to several species of insects.

Although a large number of workers are at present engaged in the search for synthetic organic insecticides it has not yet been possible to relate toxicity to chemical constitution to such an extent that accurate predictions as to the insecticidal value of a compound may be made from a study of its chemical constitution. Perhaps the most general statement that may be made concerning this group of compounds is that they appear to be relatively specific in their toxic action; that is, a given compound, although highly toxic to one insect species, may be innocuous to others.

Meanwhile the search for new organic insecticides continues. It is yet too early to make sweeping predictions, but this line of approach to the problem of the perfect insecticide would appear to promise much for the future.

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PART II

Insecticides

CONTACT POISONS

or

ERADICANT INSECTICIDES

CHAPTER V

NICOTINE AND PYRETHRUM

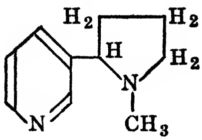
Contact insecticides are those materials which exert their toxic action upon insects directly, either through the epidermis or by some other means, as contrasted to the stomach insecticides which, to be effective, must be ingested. Theoretically, contact insecticides may be used to control nearly every variety of insect; they are particularly useful, however, against those species which feed from the exterior on the interior portion of a plant, or those which for some reason will not ingest a toxic material distributed over the area frequented by them. Substances which act as ovicides are usually classified as contact poisons.

NICOTINE

Preparations made from the tobacco plant have been used as insecticides for nearly two centuries. Both water extracts and the powdered leaves themselves were used, and exhibited high toxicity against certain species of insects, particularly the aphids. The use of tobacco against soft-bodied insects was, therefore, well established before the discovery, by Posselt and Reimann in 1828, of nicotine as the active alkaloidal principle of tobacco. The use of nicotine as an insecticide, both as tobacco preparations and as concentrated preparations of the alkaloid itself, has continued, and at present it is one of the most valuable and widely used of the insecticides. During 1938 it was estimated [1] that over 3,000,000 pounds of nicotine sulfate were used as an insecticide.

Commercially, nicotine is produced from two sources: the ordinary tobacco of commerce, *Nicotiana tabacum* Linn., and a coarser species, cultivated for human use only by certain native tribes, *Nicotiana rustica* Linn. The nicotine from *N. tabacum* is extracted from the coarse portions of the plant, such as stems and leaf midribs unsuited for the manufacture of smoking or chewing tobacco. *Nicotiana rustica*, on the other hand, contains a high percentage of nicotine, and is cultivated as a source of the alkaloid in Russia.

Chemistry of Nicotine. Nicotine is an alkaloid, 3-(1-methyl-2-pyrrolidyl) pyridine with the following structural formula:

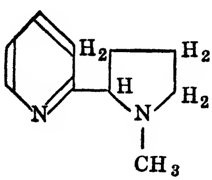


Nicotine (β — form)

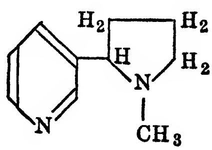
The alkaloid was first synthesized by Pictet and Rotschy [2] in 1904. The naturally occurring alkaloid is laevorotatory, although the salts of nicotine are dextrorotatory. The pure alkaloid is a colorless, odorless liquid with a boiling point of 247.3° C. Upon standing, nicotine darkens in color, becoming more viscous at the same time. Solutions of some age are dark brown or nearly black.

Since nicotine is a basic compound, it forms salts with acids. Of these, the most important from an insecticidal standpoint is the sulfate, in which form most of the alkaloid is at present sold. Nicotine is isolated from tobacco waste—largely stems—by steam distillation, and is sold commercially as a solution containing 40 per cent of the base. Free nicotine is also available, and is sometimes used, particularly in England; but because it occasionally causes illness among those applying the sprays, the sulfate is preferred, as this is considerably less toxic to man.

Two position isomers of nicotine are possible, as well as the optically isomeric forms already mentioned. The two forms have been called α- and β-nicotine, respectively. The form commonly found is β-nicotine. Craig [3] and Oosterhuis and Wibaut [4] have



α - nicotine



β - nicotine

described the synthesis of α-nicotine, and Richardson, Craig, and Hansberry [5] have reported toxicity tests of the various forms of the

alkaloid. These authors report that when solutions of the nicotines were applied to *aphis rumicis* under standard conditions, l-β-nicotine was most toxic, followed by the racemic dl-β-nicotine, and with the dl-α-nicotine showing much less toxicity. The laevo form (l) of β-nicotine was almost exactly twice as toxic as the dl-form, indicating little or no toxicity for the dextrorotatory form. Macht and Davis [6] have also found the β-nicotine to be much more toxic to vertebrates than the α form, and in another paper [7] report the same relative toxicities when applied to seedlings of *Lupinus albus*.

Compounds of Nicotine. Richardson and Shepard [8] found that nicotine as the free base was from 5 to 7 times as toxic as nicotine sulfate or hydrochloride when tested against mosquito larvae, but Starr and Richardson,[9] comparing l-nicotine d-tartrate against l-nicotine, found the former to be slightly (possibly not significantly) more toxic than the latter. Because most waters used in the preparation of spray mixtures are slightly alkaline, and because nicotine is commonly used in combination with a soap which produces an alkaline solution, it is probable that nicotine sulfate reaches the insect in most cases as the free base. Several workers have found that the efficiency of nicotine sulfate sprays increases as the alkalinity of the spray water is increased.

Of the chemical combinations of nicotine, the combination of oleic acid and nicotine suggested by Moore,[10] and others of a similar nature were investigated by Hoyt.[11] Such compounds, however, have never been widely used as insecticides, possibly because of more or less rapid deterioration, which results in the formation of an insoluble resinous condensation product.[12] The tannate has been used frequently as a substitute for arsenicals in late sprays applied to apples, but it has been the general opinion that its relatively high cost and inferior protection will not permit it completely to supplant lead arsenate as a spray material for the codling moth.

Nicotine silicotungstate, dimethyl nicotinium sulfate, and nicotine bitartrate were investigated by Swingle and Cooper,[13] who found that the silicotungstate was effective against several species of lepidopterous larvae. The bitartrate was nearly as effective as the silicotungstate, but it was water-soluble, while the dimethyl nicotinium sulfate, used in these experiments with bentonite,

was least effective. Austin, Jary, and Martin [14] tested a long chain nicotinium bromide, "Tinocine D" (British patent 401,707), and found that it had approximately the same insecticidal value as nicotine itself.

Hansberry and Norton [15] have reported the insecticidal properties of a number of compounds of nicotine against *A. rumicis* L. These may be divided into groups having similar chemical constitution or physical properties:

A. Nicotine alginate
" Aresket
" caseinate
" humate

B. Nicotine $CuCl_2$ double salt
" $ZnCl_2$ " "
" $SnCl_2$ " "

C. Nicotine laurate
" oleate
" linoleate
" stearate
" naphthenate

D. Nicotine peat
" bentonite
" silicotungstate
" Reineckate
" resorcinol-formaldehyde
" cuprocyanide

E. Dodecyl nicotinium iodide
Didodecyl nicotinium diiodide
Dodecyl nicotinium bromide
Didodecyl nicotinium dibromide

The nicotine Aresket was apparently a compound of nicotine with an alkyl phenyl benzene sulfonic acid. The laurate, oleate, and linoleate were liquids, the stearate a waxy solid. Nicotine Reineckate was prepared from ammonium thiocyanate and ammonium dichromate.

Of these compounds, Hansberry and Norton found the fatty and naphthenic acid compounds to have a toxicity greater than the alkaloid alone, plus the advantage of the wetting and spreading

action due to their soap-like nature. Group D, the insoluble nicotine compounds, showed little or no toxicity to aphids.

Nicotine Mixtures and Dusts. Because of the rapid loss of nicotine from mixtures applied to plant surfaces, various substances have been suggested to "fix" the alkaloid so that its period of usefulness may be prolonged. A combination of nicotine and peat has been suggested by Markwood,[16] and the same author has produced a nicotine humate preparation.[17] The former material is insoluble in water, while the latter is soluble. In the preparation of nicotine peat, the peat is treated with dilute acid if necessary to remove calcium and other bases, and then heated to 82° C. with a reflux condenser with the required amount of nicotine solution for a few minutes. The dried and ground powder prepared by Markwood contained approximately 10 per cent of nicotine.

Nicotine bentonite preparations which have been used for a number of years were first suggested by Smith.[18] These combinations are prepared commercially by adding the nicotine to a bentonite suspension, allowing the latter to adsorb the alkaloid, and then drying and grinding the mixture. Homemade or "tank-mixed" nicotine bentonite mixtures are also widely used. These are prepared by adding nicotine to bentonite suspensions in the tank of the spraying apparatus immediately before application. One widely used formula for the preparation of a tank-mixed nicotine bentonite spray calls for the use of one pint of 40 per cent nicotine sulfate, five pounds of Wyoming bentonite and one quart of soybean oil per 100 gallons of spray mixture. An additional wetting agent, such as sodium lauryl sulfate, may be added at the rate of one-half ounce per 100 gallons.[19]

Fahey,[20] in an extensive study of bentonites from various sources, found wide differences in sorptive powers among the samples tested. He found that the ability of the bentonite to remove nicotine from water solution was a measure of the degree of the retention of the nicotine in the spray deposit after weathering. He concluded that a bentonite suitable for use in tank-mixed nicotine bentonite preparations should have high swelling properties, should be flocculated from water suspensions by nicotine, and should exhibit a high adsorption for the nicotine from such solutions. In properly made nicotine bentonite mixtures

the alkaloid should be held very tenaciously, and is thus available as an insecticide over a considerable period of time. It should be noted that nicotine bentonite mixtures function as protective, as well as contact or eradicant insecticides.

Two materials, agar-agar and karaya gum, have been found to increase the insecticidal efficiency of nicotine solutions, and have been suggested as activators for nicotine sprays.[21, 22]

Dust mixtures containing nicotine are widely used, particularly on vegetable crops. For this purpose, finely ground tobacco diluted with a suitable carrier is often used. More common, however, are dust mixtures containing a carrier or diluent to which has been added nicotine in the form of the sulfate. Thatcher and Streeter [23] have classified the carriers for nicotine sulfate in dusts into three classes. In the first class are the sorptive materials, among which should be mentioned *kaolin*, made up in part of the mineral kaolinite, $Al_2O_3(SiO_2)_2H_2O$; *bentonite*, composed mainly of the clay mineral montmorillonite, a hydrated aluminum silicate; *pyrophyllite*, $HAl(SiO_3)_2$; *fuller's earth*, another slightly different form of hydrated aluminum silicate usually containing a higher percentage of combined water; *talc*, a magnesium silicate $H_2Mg_3(SiO_3)_4$, produced by grinding soapstone or steatite; *kieselguhr* and other related forms of diatomaceous earth, composed mainly of the siliceous remains of minute organisms. As a class these materials tend to sorb the nicotine to such an extent that the mixture becomes less useful as an eradicant or contact insecticide, although it may be of considerable use as a stomach poison. The nature of the union between the alkaloid and the carrier is not known, but it has been suggested that the base exchange properties of certain materials in the group, such as bentonite, may play an important part in the retention of the alkaloid. Since sorption is considered as a surface phenomenon the particle size of the carrier will probably determine the degree of retentiveness.

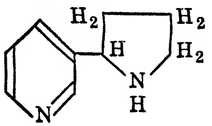
In the second class of carriers, Thatcher and Streeter group the crystalline materials which are ordinarily considered inert. These include gypsum (calcium sulfate, $CaSO_4$); sulfur; slate dust; etc. It should be noted that even these materials can exhibit sorptive properties in extremely small particles, so that it would be incorrect to consider them as completely inert under all conditions.

The third class of carriers includes the alkaline substances such as hydrated lime, $Ca(OH)_2$; calcium carbonate, either purified or in the form of finely ground limestone; and the dolomitic limes and limestones containing variable amounts of magnesium hydroxide and carbonates, respectively. These alkaline substances react with nicotine sulfate to form free nicotine, and are sometimes called the "active" carriers. Such carriers are useful under conditions where a quick-acting contact insecticide dust is desired.

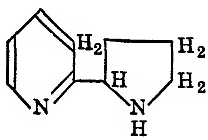
COMPOUNDS RELATED TO NICOTINE

Since nicotine contains both the pyridine and pyrrolidine nuclei, various workers have investigated other compounds having these and similar organic groupings in an effort to obtain an insecticide of wider usefulness.

The Nornicotines. These compounds, corresponding to α- and



β - nornicotine

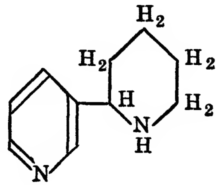


α - nornicotine

β-nicotine, respectively, are similar to the nicotines except that the methyl group attached to the pyrrolidine ring has been replaced with a hydrogen atom; they have been synthesized by Craig,[3] and Richardson, Craig, and Hansberry [5] determined their toxicity against *aphis rumicis*. These tests demonstrated that the dl-β-nornicotine was more toxic than the corresponding dl-β-nicotine, but almost equal in toxicity to (natural) l-β-nicotine. The dl-α-nornicotine and dl-α-nicotine, on the other hand, were of equal toxicity, but both were far less toxic than the racemic mixtures of the β compounds. Macht and Davis,[7] using the same compounds on seedlings of *Lupinus albus*, found also that the dl-β-forms of both nicotine and nornicotine were more phytocidal than the dl-α-forms, but in contrast noted that the dl-nornicotines (both β- and α-forms) were more phytotoxic than the corresponding nicotines. The differences between the phytocidal effectiveness of the α and β forms was not so great as the insecticidal differences reported by Richardson, Craig and Hansberry.

Smith [24] has recently reported that l-nornicotine occurs naturally in *Nicotinana sylvestris*, a species of tobacco. In this plant it composes about 95 per cent of the alkaloids present, with the remainder nicotine.

Anabasine (Neonicotine). This compound, 3-(2-piperidyl) pyridine, was first found to have insecticidal value by Richardson and



Anabasine (Neonicotine)

Smith,[25] who observed the insecticidal action of crude dipyridyl oil, which contained six possible isomeric dipyridyls, of which the particular derivative having the greater toxicity was named neonicotine. Smith, Richardson, and Shepard [26] found that the toxicity of this compound against *aphis rumicis* was approximately the same as nicotine itself.

This same compound was subsequently found by Orechoff and Menschikoff [27] to be present in a weed, "itsegek," *Anabasis aphylla* Linn. The plant, a perennial of the family Chenopodiaceae, is indigenous to many areas of the semi-arid steppes of Transcaucasia, Russian Turkestan and neighboring parts of Central Asia. Farther south, it is again found in Morocco, Algeria, and Tunis. It grows from 12 to 18 inches high, and possesses a rootstock from which arise a large number of green, jointed, twig-like shoots having small, thin lateral branches bearing inconspicuous flowers. Orechoff and Menschikoff named the alkaloid anabasine. Smith [28] later proved anabasine to be identical with neonicotine, and the material now extracted from the plants is sold as anabasine.

In 1935 Smith [29] found anabasine present in the leaves and roots of the tree tobacco, *Nicotiana glauca*, growing in the southwestern United States. This species not only contains the alkaloid anabasine, but is rich in citric and malic acids.

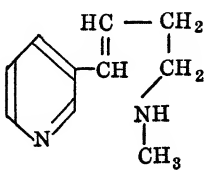
Nelson [30] found that the crude anabasine sulfate of commerce appeared to be a mixture of alkaloids, among which have been reported: aphillidine, $C_{15}H_{22}ON_2$, m.p. 112–113° C.; aphylline, $C_{15}H_{24}ON_2$, m.p. 52–53° C.; lupenine, $C_{10}H_{19}ON$, and methylanabasine. The crude anabasine sulfate available commercially contains approximately 40 per cent total alkaloids, of which about 70 per cent is anabasine, the remainder the alkaloids mentioned above.

Campbell and Sullivan [31] have found that lupenine and methylanabasine have less insecticidal action against mosquito larvae than nicotine or anabasine itself.

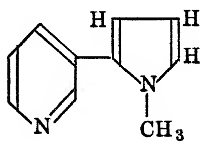
Anabasine was found by Richardson, Craig, and Hansberry [5] to be much more toxic to *aphis rumicis* than l-β-(natural) nicotine. A concentration of only 5 mg. per 100 cc. of anabasine was required to produce 50 per cent mortality, while the two next most effective compounds tested, dl-β-nornicotine and l-β-nicotine, required concentrations of 45 and 49 mg. per 100 cc., respectively. As an aphicide, commercial anabasine sulfate thus appears to be equal or superior to nicotine sulfate.

Anabasine may be distinguished from nicotine by the fact that it is precipitated from methyl alcohol solution as the silicofluoride, while nicotine remains in solution. It is said that an ether solution of iodine precipitates ruby red needles of periodide ($C_{10}H_{14}N_2I_2HI$) from ether solutions of nicotine, while anabasine does not react.

Other Related Compounds. Richardson and Shepard [32] found that metanicotine, in which the pyrrolidine ring is broken, had considerably less toxicity than nicotine. Nicotyrine, in which the pyrrolidine ring is replaced by the pyrrole ring, had approximately the same toxicity as metanicotine; that is, 7 to 10 times less toxic than nicotine.



Metanicotine



Nicotyrine

These authors tested the insecticidal properties of a considerable number of compounds related to nicotine, but found only the two mentioned to approach nicotine in toxicity. Their work throws considerable light, however, on the mechanism of toxic action.

LaForge,[33] and Tattersfield and Gimingham,[34] in preliminary tests of benzylpyridine, indicated that this compound might hold promise as an insecticide. Richardson and Shepard [32] found, however, that the toxicity of this substance was relatively low.

Starr and Richardson [9] have reported tests with optically active forms of α-p-tolylpyrrolidine. When applied to aphids as the tartrates, both the laevo and dextro forms showed thirty times less toxicity than l-nicotine.

PYRETHRUM

The date of the first use of pyrethrum preparation as an insecticide is unknown; it probably was used by Caucasian tribesmen at an early date, but its source was apparently kept a secret until an Armenian named Jumtikoff learned that the powder used

FIG. 2. Field of young pyrethrum plants growing near Belleville, Penn. Courtesy Dr. R. E. Culbertson.

as an insecticide was obtained from the flower heads of certain species of pyrethrum. In 1828, using this knowledge, Jumtikoff's son began the manufacture of the powder on a large scale.[35] Gnadinger,[36] in his excellent book, states that the use of pyrethrum

flowers for insecticidal purposes originated in Persia, from which place it was introduced into Europe early in the nineteenth century. Pyrethrum was introduced into the United States about 1855; consumption grew rapidly, 600,000 pounds being used in 1885, 3,000,000 pounds in 1919. In 1939, 13,569,400 pounds valued at $3,173,635 were imported into the United States.[37]

The first use for pyrethrum (sometimes called Trieste) flowers was as an insect powder, particularly against household insects where an insecticide non-toxic to warm-blooded animals is particularly desirable. About 1916, kerosene extracts of pyrethrum flowers appeared, and found extensive use as a spray,

FIG. 3. Field of mature plants (see Fig. 2).
Courtesy Dr. R. E. Culbertson.

particularly against houseflies and mosquitoes. At present, only a fraction of the pyrethrum is used as a powder; most going into the preparation of extracts. There are said to be nearly 2000 brands of pyrethrum-base household sprays on the market in this country at present.[38]

The insecticidal principle in pyrethrum is found in the flower head of certain plants of the *Chrysanthemum* genus, family *Compositae*. Only a few species of this rather large family are valuable as insecticides. Three species are recognized by the United States Department of Agriculture as suitable for insecticidal use. These

are: *Chrysanthemum* (*Pyrethrum*) *roseum* Web. and Mohr.; *C.* (*P.*) *cinerariaefolium* Trev.; and *C. Marshalli* Ach. (*P. carneum* Bieb.). Of these three forms, *P. cinerariaefolium* is by far the most important commercially. The so-called African or German pyrethrum, derived from the roots of *Anacyclus pyrethrum* D. C. and *A. officinarum* Hayne, and at one time used medicinally under the name "pyrethrum root" or "pellitory root" is in no way related to the insecticide and should not be confused with it.

Chrysanthemum cinerariaefolium is a herbaceous perennial growing from 18 to 24 inches tall. The flower heads comprise a disc of yellow tubular florets borne on a rounded receptacle and encircled by a row of white or cream ray florets. Below the latter is an involucre composed of three rows of overlapping scales, which enclose the flower head in the bud stage. It appears that the maximum pyrethrum content is reached in the flower head at about the time the flower becomes fully open.

The flowers are harvested by hand or mechanically, dried and baled for shipment. The active principles of the flower (pyrethrins) are lost rather rapidly from powdered pyrethrum. Weed [39] gives the following table showing the approximate losses in pyrethrins from powdered pyrethrum:

TABLE 3

LOSS IN PYRETHRINS FROM POWDERED PYRETHRUM

Initial Quality	*Per Cent Lost in 6 Mo.*	*Per Cent Lost in 12 Mo.*	*Per Cent Lost in 24 Mo.*
0.5......0.6%	9–15	12–20	.....
0.8......1.0%	10–16	16–24	30–36
1.1%....up	14–20	21–25	30–40

This loss is particularly rapid when pyrethrum is exposed to air in thin layers, as shown by Tattersfield.[40] He found that the addition of antioxidants such as hydroquinone, pyrogallol, etc., prevented this loss of toxicity to a large extent.

Up to the time of the second World War, Japan, Yugoslavia, Kenya, and Italy were the largest pyrethrum-producing countries. Since that time Kenya has dominated the market, with smaller quantities coming to this country from Brazil. In the United

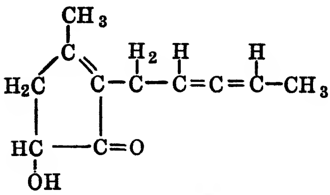
States, small plantations have been established in various areas, and in some instances have been quite successful. The amount of hand labor involved in picking, however, makes the cost high. A mechanical picker has recently been developed which may make the domestic production of pyrethrum economically possible.

FIG. 4. Flower head of pyrethrum, *Chrysanthemum cinerariaefolium.*

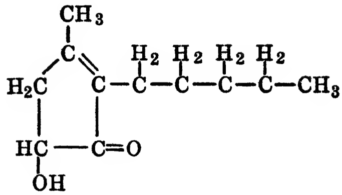
Chemistry of Pyrethrum. Until 1924, when the work of Staudiner and Ruzicka [41] was published, numerous attempts to isolate the active principle of the plant material had been unsuccessful, although Fujitani,[42] McDonnell, Roark, and Keenan,[43] and Yamamoto [44, 45, 46] had indicated that the active principle was a mixture of esters, which Fujitani called "Pyrethrone" of an alcohol "Pyrethrole." Staudinger and Ruzicka isolated a ketone alcohol, the alcoholic portion of the active esters, which they called "Pyrethrolone" (*A*). This alcohol was reduced by hydrogen in alcoholic solution, forming tetrahydropyrethrone, 3-methyl-2-amylcyclopentanone (*B*).

The acids of the ester as isolated were: chrysanthemum monocarboxylic acid (*C*) and chrysanthemum dicarboxylic acid (*D*). Pyrethrolone when esterified with chrysanthemum monocarboxylic acid yielded an active ester, called by Staudinger and Ruzicka, "Pyrethrin I" (*E*). Pyrethrolone, when esterified with chrysanthemum dicarboxylic acid, did not yield an active ester, but when the monomethyl ester of chrysanthemum dicarboxylic acid was combined with the alcohol the resulting compound was

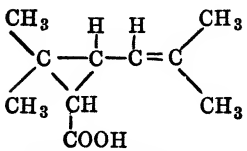
almost as active as pyrethrin I. This compound was called "Pyrethrin II" (*F*).



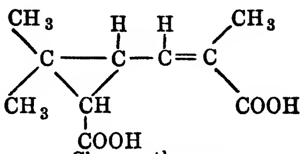
Pyrethrolone (A) *



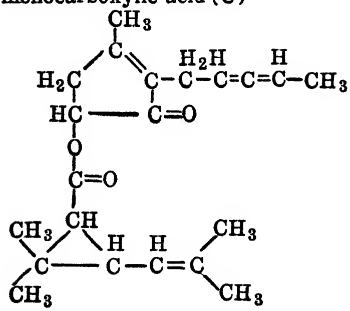
Tetrahydropyrethrone (B)*



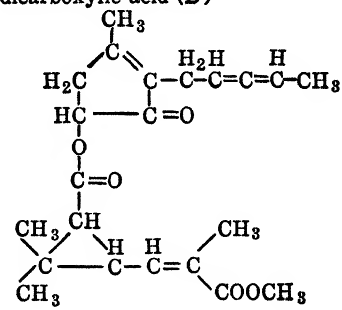
Chrysanthemum monocarboxylic acid (C)



Chrysanthemum dicarboxylic acid (D)



Pyrethrin I* (E)



Pyrethrin II* (F)

These compounds are both viscous liquids, pyrethrin I boiling at 150° C. under vacuum, pyrethrin II decomposing when distilled in vacuum. The pyrethrins are soluble in a variety of organic solvents, but not in water, in which they are said to exist in colloidal suspension. Both pyrethrins are toxic to insects, although Staudinger and Ruzicka, and Tattersfield, Hobson, and

* The original formulas for pyrethrolone and tetrahydropyrethrone given by Staudinger and Ruzicka have been modified by La Forge and Haller.[47, 48, 49] Since these appear to be the correct formulas, they are given here, to avoid confusion. The original formula differs from those given in having two additional hydrogen atoms, in the 2,3 position in the nucleus, thus giving a saturated ring structure. These changes obviously affect the constitution of the pyrethrins as well.

Gimingham [50] found that pyrethrin I is more toxic to cockroaches and aphids than pyrethrin II. This has been confirmed by other workers on other insects. Ripert and Gaudin,[51] however, found pyrethrin II more toxic than pyrethrin I to frogs, fish, and mice.

As mentioned previously, pyrethrum extracts, usually in kerosene, are widely used as sprays against houseflies; and within recent years considerable work has been done with pyrethrum preparations as insecticides for use on field crops. They are apparently effective both as sprays and as dusts, particularly on vegetable crops where the monetary return per acre is relatively high, and the presence of a poisonous residue is undesirable from the point of view of human health.

Derivatives of the pyrethrins have been prepared by several investigators. Haller and Sullivan [52] prepared the hydrogenated derivatives, and, testing them against the housefly, found that mild catalytic hydrogenation destroyed the greater part of the toxic action of the pyrethrins. Harvill [53] prepared the lauryl, myristyl, cetyl, and diethanolamine esters of chrysanthemum monocarboxylic acid. He found that these derivatives were about 90 per cent as effective against *aphis rumicis* as the pyrethrins at the same concentration.

Pyrethrum is not compatible with alkalies, because, being an ester, it is easily hydrolyzed. For this reason Roark [54] has pointed out that soaps should not be compounded with pyrethrum or pyrethrum extracts.

Preparation of Pyrethrum Insecticides. As mentioned previously, pyrethrum was first used as an insecticide in the powdered form. In fact the term "insect powder" has legally come to mean pyrethrum powder, and no other material may be so designated. The powdered pyrethrum flowers may be used directly as dusts, either alone or diluted with a suitable carrier such as hydrated lime or dusting sulfur. Such mixtures give fairly good results, but are not particularly efficient, since a large part of the pyrethrin content is held within the unbroken cell walls of the plant material and thus is largely wasted.

More economical use of the active insecticidal principles may be obtained by first extracting them from the flowers with a solvent such as kerosene or alcohol, and then mixing this extract with a finely divided carrier. The solvent may or may not be allowed to

evaporate. Each particle of the dust thus becomes coated with the pyrethrins, and the mixture is highly efficient as a contact insecticide. A variety of carriers has been used for the preparation of such dusts, including diatomaceous earth, powdered charcoal, pulverized pyrethrum marc, talc, gypsum (calcium sulfate), and bentonite. With bentonite, as well as with some of the other more highly adsorbent materials, the pyrethrins are held rather tenaciously, and are apparently released more slowly than from more inert carriers, such as gypsum and talc. When kerosene is used to produce the extract, the solvent is often retained in the final mixture, and functions to protect the pyrethrins from decomposition.

Dust concentrates may be made from concentrated pyrethrum extracts prepared with a nonvolatile solvent and a suitable adsorbent carrier. These dust concentrates are diluted before use with an inert diluent. Antitoxidants such as tannic acid, hydroquinone, or some synthetic organic compound as 1,4-toluidoanthraquinone are sometimes used to stabilize the pyrethrins in dust preparations. The pyrethrum oleoresins, freed from solvent, have been used to mix with dust carriers, but such combinations are not common.

For horticultural sprays, concentrated extracts of pyrethrum in acetone, alcohol, or a hydrocarbon solvent together with an emulsifier are on the market. For use as sprays these are diluted with water to form suspensions or emulsions. The destructive action of alkalies on the pyrethrins has already been mentioned. It appears, however, that non-aqueous concentrates of pyrethrum extracts and soap do not deteriorate rapidly, although decomposition is rapid after dilution with water.

By far the greatest use of pyrethrum as an insecticide is in household fly and mosquito sprays. These are made in two ways. By the older method the coarsely ground flowers are extracted with a light hydrocarbon oil. Highly refined "odorless" kerosenes are ordinarily used for this purpose. These extracts are usually diluted to a uniform pyrethrin content of approximately 0.10 per cent. Rotenone is sometimes added to household sprays, as well as perfumes to improve the odor, and antioxidants and stabilizers to assist in the preservation of the pyrethrins. Livestock sprays are similar in composition to household sprays, ex-

cept that slightly heavier hydrocarbon oils are usually used, and repellents such as pine oil are sometimes added.

In the second method commonly used for the preparation of household sprays, an extract of the oleoresins and pyrethrins is first made in a solvent such as ethylene dichloride. The solvent is then removed, and the semi-solid residue diluted with kerosene or other hydrocarbon solvent. More efficient extraction of the flowers can be obtained in this way, and the process lends itself more readily to the commercial preparation of sprays, since the concentrates may be purified and standardized and shipped with greater economy than the more dilute hydrocarbon extracts.

Certain chemicals have been found to increase the insecticidal action of pyrethrum sprays. Among these should be mentioned Yarmor Pine Oil, ethylene glycol ether of pinene, and fenchyl thiocyanoacetate (U. S. patents 2,209,184 and 2,217,611). These compounds were found to be efficient "activators" by Mentzer, Daigh and Connell.[55]

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CHAPTER VI

ROTENONE AND MISCELLANEOUS ORGANIC COMPOUNDS

Rotenone and the Fish-Poison Insecticides

The use of decoctions of various plants as fish poisons has been practiced for many centuries, particularly by native tribes in the East Indies, Africa, India, and South America. Roark [1] cites several references to published descriptions of this practice prior to the year 1800, the first recorded reference being in 1665. The procedure usually used by the natives to poison fish was to macerate the poisonous plants with water and to pour the decoction into a selected body of water and to collect the fish which rose to the surface. The fish so procured were perfectly edible. Many species of plants have been used as fish poisons.

Oxley [2, p. 651] recommended the use of a decoction of tuba root for controlling insects attacking nutmeg trees in Singapore in 1848. His mention was casual, as though at that time the material were a commonly used insecticide. There is considerable evidence that the Chinese used tuba as an insecticide at a very early date. It was not until about 1920, however, that the use of these plant products as insecticides became common, but since that time consumption of the plants of this group having insecticidal properties has increased by leaps and bounds, so that in 1939 over four million pounds of cube and derris roots were imported into the United States.

The reason for this popularity is not hard to find: rotenone and related substances (the active principles of the fish-poison insecticides) are, like pyrethrum, relatively harmless to warm-blooded animals, and at the same time are efficient insecticides. They have no appreciable effect, moreover, on the plants to which they are applied, thus being in many respects the ideal insecticides.

Sources of the Rotenone Group of Insecticides.* At least four

* Roark has recently proposed that the word "rotenoids," first used by Buc, be applied to those substances other than rotenone, but structurally related to it, naturally occurring in leguminous fish-poison plants. (Jour. Econ. Entomol. 33: 416. 1940.)

genera of plants are known to be used as fish poisons, and certain species of each genus have been found to have insecticidal properties. Listed in the order of their importance as insecticides they are:

1. *Derris* (*Deguelia*). Roark [3] lists 30 species of *derris*, distributed among the tropical regions of the world. Of these species *D. elliptica* is by far the most important as a source of insecticides, being cultivated in British Malaya and the Netherlands East Indies, although much of the earlier importations were the roots of wild plants. This species is known by a variety of common

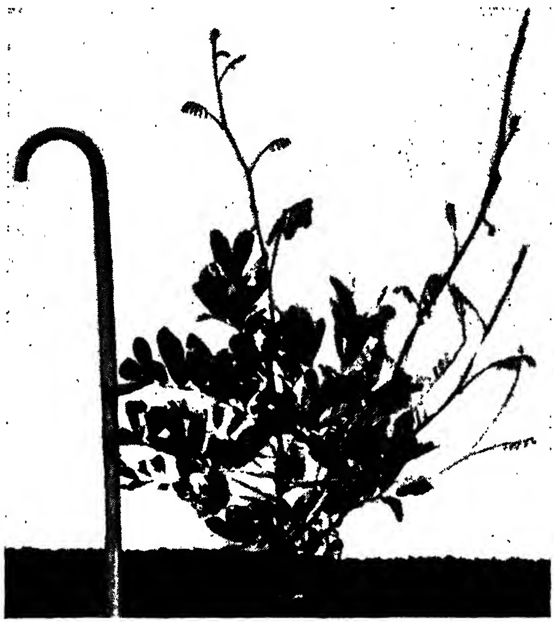


FIG. 5. Young tuba (*Derris elliptica*) plant. Courtesy Dr. C. M. Smith.

names, the most common being *tuba* or *toeba*. *D. malaccensis* is also the source of some insecticidal material, and is known by the same common name. The roots of both of these species contain the active principles.

Selection and breeding has in the past few years raised the rotenone content of certain varieties of this species so that as much as 13 per cent of rotenone has been found in certain clones,

with a total ether extract of over 30 per cent, both on moisture-free basis.

FIG. 6. Export bale of tuba (*Derris elliptica*) root as prepared in Java. Courtesy Dr. C. M. Smith.

According to Holman,[4] some 2,334,080 pounds of derris were imported into the United States in 1939 from the following sources:

British India	11,200	pounds
British Malaya	1,877,120	"
Netherlands East Indies	183,680	"
Phillipines	228,480	"
French Indo-China	33,600	"

2. *Lonchocarpus.* This genus of tropical leguminous trees and shrubs is found mainly in the Western hemisphere, including Mexico, Central and South America, although certain species are found in Africa and Australia. Roark [5] lists seven species, of which four were known to possess insecticidal properties, while the other three were suspected of having such properties. The species commonly imported into this country for insecticidal purposes are *L. nicou*, *L. utilis*, and *L. chrysophyllus* Kleinh. A certain amount of confusion exists in the naming of the plants used, and often the identity of a particular sample of roots is difficult to establish. This is particularly true because the colloquial names for the plants apply to several species of plants, and often to plants of different genera.

These local names are: *Barbasco,* used as a general word for fish-poison plants in Spanish-speaking countries, and usually applied to *L. nicou; cube* (pronounced KOOBAY), used in Peru to designate the same species, as well as others, including *Tephrosia toxicara* [6]; *haiari,* the word used in British Guiana to designate certain species of *Lonchocarpus,* including *L. nicou; nekoe,* (*nicou*), used to designate the same general group of plants in French and Dutch Guiana, and finally *timbo,* used to designate the fish-poison plants as a group in Brazil and Ecuador.

FIG. 7. Timbo macquinho (*Lonchocarpus nicou*) one year old, grown near Para, Brazil. Courtesy Dr. C. M. Smith.

Holman [4] states that 1,906,240 pounds of *Lonchocarpus* root were imported into the United States during 1939, from the following sources:

Brazil...........	145,600	pounds
Peru.............	1,639,680	"
Venezuela........	120,960	"

3. *Tephrosia* (*Cracca*). This genus is composed of herbaceous plants and shrubs distributed over most of the world. Roark [7] lists 20 species of *Tephrosia* which have been tested as insecticides, of which 8 were found to have considerable insecticidal value. Tattersfield, Gimingham and Morris [8] found that the seeds and leaves of *T. Vogelii* contained the insecticidal principles, as did the roots of *T. toxicaria.*[9]

At present, no great quantity of *Tephrosia* species are used in this country as insecticides, although the discovery that the plant known as Devil's Shoestring, *T. virginiana* L., common in the

eastern and southern United States, contained considerable quantities of rotenone in the woody portion of the root has caused considerable interest. Sievers et al [10] have summarized the literature recently in this connection. The common names for the fish-poison plants are the same as those of the *Lonchocarpus* species, namely, *timbo, cube* and *barbasco.*

FIG. 8. *Tephrosia* (*Cracca*) *virginiana*, 19 months old, showing most of the root system. This plant yielded one pound of dried roots. Courtesy Dr. C. M. Smith.

4. *Mundulea*. The species *M. suberosa* have been investigated by Worsley.[11] These shrubs are native of tropical East Africa and India, and the toxic principles appear to be present in the bark and seeds, although it is not an important source of insecticidal material.

It is to be noted that all of the genera noted above are leguminous (fabaceous) plants. Other fish-poison plants have been reported, although their toxic principles have not been fully examined. These include species of *Milletia*, investigated by Tattersfield and Gimingham,[12] and *Spatholobus roxburghii*, a tropical climbing vine. McIndoo and Sievers [13] report insecticidal tests on some 232 preparations made from 54 species of plants reported to possess insecticidal properties.

Preparation of Insecticides from Fish-poison Plants. The rotenone content of different samples of rotenone-bearing roots is rather variable. Roots from cultivated plants of *Derris elliptica* may contain over 13 per cent rotenone, with 30 per cent of ether-soluble material; Philippine derris root averages 4 to 5 per cent rotenone. *D. malaccensis* roots contain little or no rotenone, but up to 19 per cent ether extractives: much of the dried roots of the *Lonchocarpus* species contain from 8 to 10 per cent of rotenone. Commercial preparations of cube, timbo, and derris in the United States are usually blended to produce a powder containing between 4 and 5 per cent rotenone.

For dusting purposes, the commercial powdered root is finely ground and diluted with a suitable carrier to a concentration of approximately 1 per cent. Carriers most frequently used are talc and clays of various kinds. Impregnated or coated dusts are also used. To produce these, the dried roots are extracted with a suitable solvent, such as chloroform, the extract thus produced mixed with a finely divided diluent or carrier, and the solvent evaporated. Each particle of the carrier thus becomes coated with some of the insecticidal material. This method has the advantage of even distribution of the toxic material throughout the entire mass of dust. Moreover, the size of the individual particles of the carrier may be more closely regulated than is possible with a woody, fibrous material such as the roots, which are often difficult to grind. Walnut shell flour, pyrethrum marc, clays, and other carriers and adsorbents have been used in the preparation of coated dusts. As mentioned in the discussion of nicotine dusts (p. 58), the particle size of the carrier and the degree of tenacity with which the sorbed insecticide is held will determine the readiness with which the active principles are liberated after application as insecticides.

For use as sprays, the fresh roots may be beaten to a pulp in water and the milky liquid employed as thus prepared. This was the original method employed by the natives of the Malay Peninsula but since it depends upon the use of fresh plant material it is hardly practical on a commercial scale. One of the more common methods of preparing sprays is to mix the finely ground roots with water and to apply this suspension directly. Non-aqueous extracts of the rotenoid materials are probably most widely used,

however. Among the solvents used for the preparation of such extracts, Jones and Smith [14] list the following in order of their dissolving power for rotenone: chloroform, ethylene dichloride, trichloroethylene, chlorobenzene, ethylene chlorhydrin, and benzene. Carbon disulfide, ethyl formate, and ethyl acetate are also relatively good solvents for the rotenoids. To secure the most efficient extraction, the dried rotenone-bearing plant material is ground and subjected to exhaustive extraction with one of the more efficient solvents. Such extracts may be diluted with water, the active principles then being precipitated as colloidal suspensions. More commonly, however, the concentrated extracts are diluted with a refined oil such as kerosene or light lubricating oil with the addition of a mutual solvent. The solubility of rotenone in a highly refined kerosene, for example, may be increased from about 0.05 per cent to about 0.20 per cent by the addition of a suitable mutual solvent.[15] Many of the household and cattle fly sprays on the market contain rotenoid materials dissolved in a paraffin oil with the assistance of a mutual solvent such as acetone, safrol, high-boiling ethers, dibutyl phthalate, alkylphenols, etc. Concentrated mixtures containing rotenone extracts, oil, and an emulsifying agent have been proposed. These when diluted with water yield an emulsion in which the rotenone is suspended or dissolved in the non-aqueous phase.

Air suspensions (aerosols) of rotenone have also been suggested. To produce such suspensions, the rotenone-bearing roots may be burned to form a smoke, or a liquid extract of rotenoids may be sprayed upon a heated surface and thus be dispersed.

Certain substances have been found to enhance the insecticidal action of rotenone. Although little work has been reported on the subject, Pierpont [16] found that the ethylene glycol of pinene increased the insecticidal action of a petroleum base solution of rotenone against the housefly (*Musca domestica* L.). The so-called activating agents, such as peanut and soybean oils, may also act as synergists with rotenone.

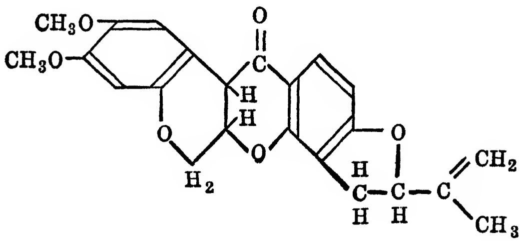
CHEMISTRY OF ROTENONE AND RELATED SUBSTANCES

A number of chemical compounds, some of them active as insecticides, have been isolated from the fish-poison plants. Rotenone, deguelin, toxicarol, and tephrosin have been isolated.

Of these, rotenone is present in the greatest amount in the majority of plants examined, particularly those of the *Derris* and *Lonchocarpus* species.

Rotenone. Nagai [17] in 1902 isolated a crystalline substance from *Derris chinensis*. Since the local name for this plant is *Rohten*, he termed the crystalline substance rotenone. A substance of similar nature had been previously isolated from *Lonchocarpus nicou* by Geoffroy,[18] and given the name nicouline. Lenz [19] in 1911 and Ishikawa [20] in 1916 also isolated an active principle from fish-poison plants, to which they gave the names "Derrin" and "Tubatoxin." Apparently these substances were all identical and the name rotenone has been adopted, although it would seem that nicouline should have been selected on the basis of priority.

The structure of rotenone was determined almost simultaneously by several investigators, including La Forge and Haller [21] who, with their associates, had been working on the problem for several years. For a detailed discussion of the determination of the structure of rotenone see La Forge, Haller, and Smith.[22] The formula is given below:



Rotenone

Pure rotenone crystallizes from alcohol in white six-sided plates belonging to the orthorhombic system. The melting point is 163° C.,* and solutions in organic solvents are levorotatory. As mentioned previously, rotenone is relatively soluble in the chloro-organic solvents, with the exception of carbon tetrachloride. It is practically insoluble in water (about 1 part in 6,000,000 parts), and only slightly soluble in the petroleum oils.

* Two enantiotropic forms of rotenone are known to exist, with melting points at 163° C. and approximately 180° C., respectively. The lower melting compound is the common one. See J. Amer. Chem. Soc. **57**: 2616–2618 (1935).

It is to be noted that the rotenone molecule consists of three characteristic systems—a central dihydro-γ-pyrone, flanked on one side by a dihydrobenzopyran and on the other by a dihydrobenzofuran system. Although the rotenone molecule contains three

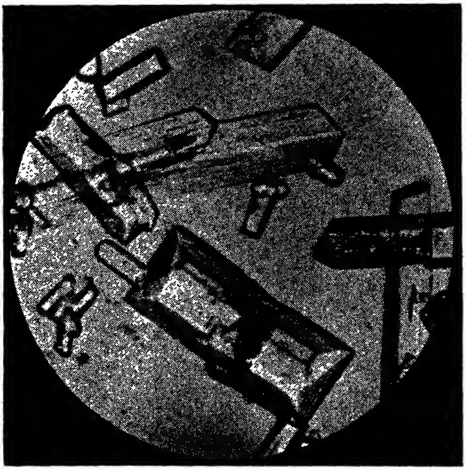


FIG. 9. Dimorphic form of dihydrorotenone, m. p. 164° C. 60 ×. Courtesy Dr. C. M. Smith.

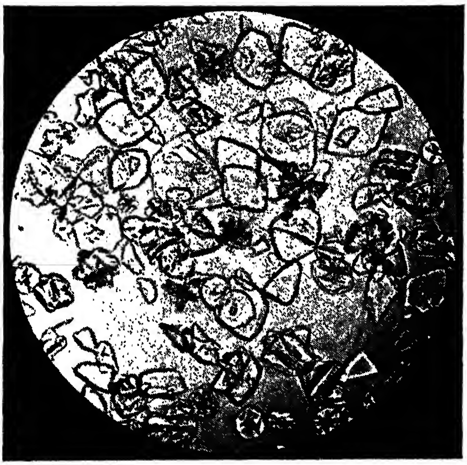


FIG. 10. Dimorphic form of dihydrorotenone, m. p. 216° C. 60 ×. Courtesy Dr. C. M. Smith.

asymmetric carbon atoms, and eight optical isomers should be possible, only one is known.

When exposed to light and air, rotenone undergoes decomposition. Colorless solutions of rotenone in organic solvents when

so exposed become successively yellow, orange, and finally deep red as a result of oxidation, and may deposit crystals which contain dehydrorotenone and rotenonone, two products which are not toxic to insects.[23, 24] Thin deposits of rotenone on plants exposed

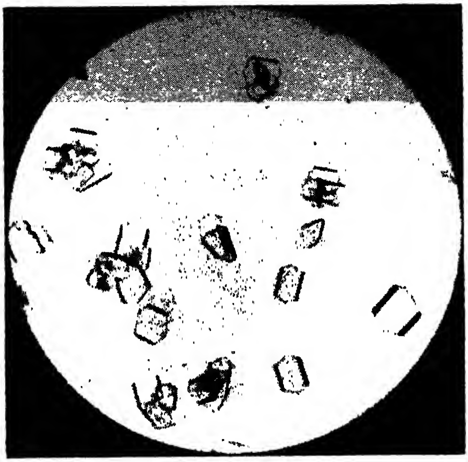


FIG. 11. Rotenone crystallized from alcohol. 55 ×.

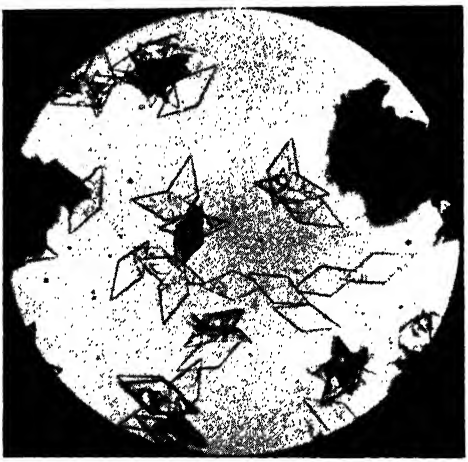


FIG. 12. Rotenone crystallized from acetone. 55 ×.

to air and light change color in about 10 days. This change may be retarded by the addition of lampblack to the spray, thus excluding the light from the deposit.[24]

Rotenone, when crystallized from certain solvents, contains definite amounts of the solvent in the crystal, similar to water of

crystallization in inorganic salts. These are called solvates, and contain one molecule of solvent of crystallization when crystallized from chloroform, benzene, and carbon tetrachloride; when crystallized from acetic acid, two molecules of solvent of crystallization; and none when crystallized from acetone, ethyl alcohol, ethyl acetate, and ethylene dichloride.[25] The crystal forms of three of these solvates are shown in Figs. 11, 12, and 13.

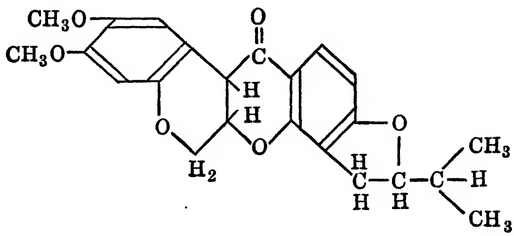
FIG. 13. Rotenone crystallized from benzene. 55 ×.

Rotenone Derivatives. La Forge and associates in a series of papers have reported the preparation and properties of a large number of derivatives of rotenone. Many of these compounds have been tested for toxicity by Gersdorff [26, 27, 28, 29] using goldfish as the test animal, and following the procedure described by him.[30] Among the compounds tested were isorotenone, dihydrorotenone, rotenone hydrochloride, acetylrotenone, acetyldihydrorotenone, rotenolone, dihydrorotenolone, acetylrotenolone, and acetyldihydrorotenolone.

Gersdorff states [29] that "each change in chemical constitution effects a characteristic change in toxicity independent of the effect of any other change. The dihydro derivatives produced by saturation of the double bond in the side chain with hydrogen have 1.5 times the toxicity of the corresponding unsaturated compounds. The acetates, whether of the enol type or the acetyl derivatives of the hydroxy compounds, have 0.56 the toxicity of the parent com-

pounds. The hydroxy derivatives have 0.10 the toxicity of the parent compounds."

The dihydrorotenone, which was found to have 1.5 times the toxicity of rotenone itself against goldfish, is characterized by the saturation of the double bond in the side chain with hydrogen. The formula thus becomes:



Dihydrorotenone

Dihydrorotenone is said to be more stable than rotenone, and yet is an efficient insecticide.[31]

Isorotenone differs structurally from rotenone in the position of the double bond: in rotenone this bond is in the aliphatic side chain attached to the five-membered ring; in isorotenone the double bond is within this ring. Isorotenone derived from rotenone is optically active, and was found to be more toxic to culicine mosquito larvae than the optically inactive form of the same compound.

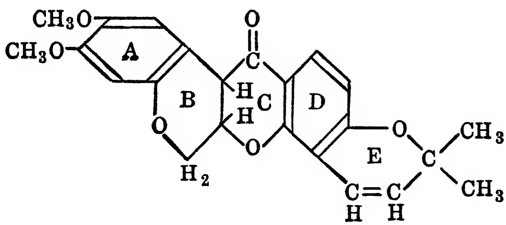
When subjected to mild oxidation, rotenone is converted to dehydrorotenone, $C_{23}H_{20}O_6$, which when boiled with alcoholic KOH and zinc dust yields a hydroxy acid, $C_{23}H_{24}O_8$. When this is oxidized with H_2O_2 in alkaline solution, a more complete breakdown takes place, resulting in the formation of derric acid, $C_{12}H_{14}O_7$. This contains the two methoxyl groups originally in rotenone, and represents one-half of the rotenone molecule.[32]

These products are not valuable as insecticides.

Deguelin—($C_{23}H_{22}O_6$). When derris or cube roots are extracted with a suitable organic solvent, and the resulting extract concentrated, most of the rotenone crystallizes out readily. The uncrystallizable residue remaining after the removal of the rotenone was found to be highly toxic to goldfish.[33] This residue contains

deguelin, toxicarol, and tephrosin, the latter probably being formed by oxidation of deguelin. When an alcoholic solution of the uncrystallizable, resinous residue is made slightly alkaline, deguelin and toxicarol separate out as an optically inactive crystalline mixture from which the two compounds may be isolated.

The compound deguelin was first isolated in 1931 by Clark [34] as a pale green substance, crystallizing in rodlike plates, and having a melting point of 171° C. Its formula is:



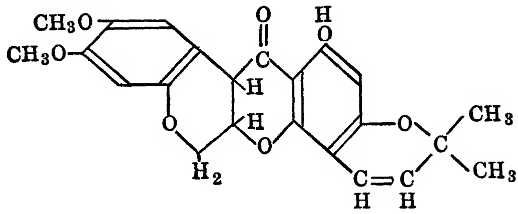
Deguelin

The great similarity between the constitution of deguelin and rotenone is at once apparent, the only difference in composition being in the configuration of ring *E*. In rotenone this ring is a substituted dihydrofuran nucleus, while in deguelin it is a 2-substituted alpha pyran ring. Since there are two asymmetric carbon atoms in the deguelin molecule, four optical isomers are possible, although none is known to exist in the crystalline form.

Deguelin, like rotenone, contains two hydrogen atoms which are readily removed by mild oxidation. A double bond is thus introduced in the molecule between the carbon atoms shared by rings *B* and *C* and the product is dehydrodeguelin, $C_{22}H_{20}O_6$.[35] The rupture of the double bond in ring *E* of the deguelin molecule, followed by the addition of two hydrogen atoms, results in the formation of dihydrodeguelin. Fink and Haller [36] tested the toxicity of the optically active and inactive forms of dihydrodeguelin against culicine mosquito larvae, and found the optically active form to be the more toxic. Deguelin itself was found to be less toxic than dihydeguelin and rotenone when tested in this way.

Toxicarol—($C_{23}H_{22}O_7$). This compound was also isolated by Clark [37] from *Tephrosia toxicara*. It is a yellow crystalline material

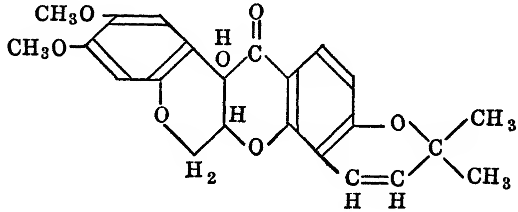
with a melting point of 219° C., and a structure very similar to that of deguelin.



Toxicarol

Toxicarol has since been found as a constituent of derris and cube, associated with rotenone in various amounts. Tests with goldfish by Gersdorff [38] showed toxicarol to be considerably less toxic than rotenone.

Tephrosin. A crystalline substance was isolated from the leaves of *Tephrosia vogelii* in 1907 by Hanriot,[39] with a formula $C_{31}H_{26}O_{10}$, and a melting point of 187° C., which he named tephrosin. Clark [40] in 1931, continuing his investigations on the fish-poison plants, isolated a physiologically active substance corresponding to Hanriot's tephrosin, but found that instead of being one compound, it was in reality a mixture of two, one of which was deguelin. The other material, when purified, crystallized in colorless prisms, and melted at 198° C. The melting point varied, however, with the rate of heating. Clark determined the structure of this compound and found it to be closely related to rotenone, deguelin, and toxicarol.

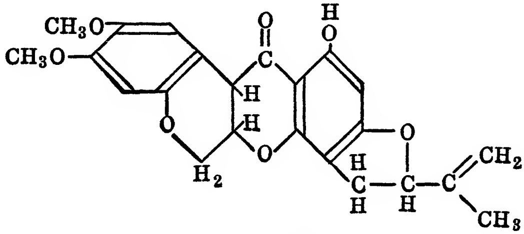


Tephrosin

Tephrosin has also been found along with rotenone and deguelin in derris and cube roots. The toxicity of tephrosin to

insects is apparently less than rotenone and deguelin, but greater than toxicarol.[41]

Sumatrol. This substance, very similar in constitution to the other compounds in this group, was isolated by Robertson and Rusby [42] from derris. It is probable that this compound has a lower insecticidal value than rotenone, to which it is closely related structurally.



Sumatrol

RESUMÉ OF THE INSECTICIDES OF THE FISH-POISON PLANTS

Five physiologically active compounds have been isolated from the fish-poison plants studied, including species of *derris, tephrosia,* and *lonchocarpus.* The quantity of each of these in the various plants examined is variable, and apparently depends to a certain extent upon the environmental conditions under which the plants are grown, as well as upon the species. Of the active principles isolated, rotenone is probably the most active as a contact insecticide, Davidson [41] giving the following order of toxicity to *Aphis rumicis:* Rotenone, 400; deguelin, 40; tephrosin, 10; and toxicarol, 1. Sumatrol has not yet been investigated as an insecticide. Rotenone and sumatrol are closely related chemically, as are deguelin, toxicarol, and tephrosin, and all five are chemically similar.

MISCELLANEOUS INSECTICIDES DERIVED FROM PLANTS

Quassia. The bitter principle extracted from the bark and wood of a small branching tree, *Quassia amara* L., found in Surinam, Brazil, Central America, and the West Indies, has been used since the middle of the eighteenth century as a tonic in the treatment of dyspepsia. Just when it was discovered that this material had value as an insecticide is not known, but apparently the extract

of the plant has been used for this purpose for some time, particularly against aphids, although it has never found great favor as an insecticide in this country. The literature dealing with quassia has recently been collected by Busbey.[43]

The greater part of the quassia now available commercially is derived from a closely related plant growing in Jamaica, *Aeschrion excelsa* (Swartz) Kuntze.

The extract of quassia was tested as an insecticide by McIndoo and Sievers [44] and found to be relatively ineffective against aphids. These investigators, however, worked with aqueous extracts of the quassia wood

The bitter, and presumably the physiologically active, principles of the Surinam quassia are quassin and neoquassin, the former first isolated and named by Winckler, according to Clark,[45, 46] who has recently investigated the chemical structure of these two compounds. The first of these, when extracted with hot water and purified by recrystallization from dilute methyl alcohol, is in the form of thin colorless rods and plates, melts at 205°–206° C., and is dextrorotatory. Neoquassin, when prepared in the same manner, crystallizes as dense, colorless six-sided prisms and quadrilateral plates, melting at 225°–226° C. Both compounds have the same empirical formula, $C_{22}H_{30}O_6$, contain two methoxyl groups, and are apparently isomeric.

A third compound, picrasmin, has been isolated from *Picrasma* (*Aeschrion*) *excelsa* by Clark.[47] This material has been isolated and named previously by Massute. Picrasmin has the same empirical formula, $C_{22}H_{30}O_6$, as quassin and neoquassin, but crystallizes in thin, colorless plates and occasional rods which melt at 218° C. It is dextrorotatory, and, like the other two compounds, contains two methoxyl groups.

While little is known as to the insecticidal properties, these three compounds, closely related among themselves, would appear possibly to be related to rotenone.

Croton. Used as an insecticide in China, the seed of the croton tree, *Croton tiglium* L., was mentioned by McIndoo and Sievers,[46] but not tested by them. Croton seeds apparently contain a vesicant principle which, according to Spies,[49] was relatively toxic to goldfish.

Miscellaneous Plant Materials. Many other species of plants have been reported to be potential sources of insecticidal materials. In addition to quinine and cinchonine, other alkaloids are present in various species of *Cinchona,* some of which have been used as insecticides. Larkspur, from which come the *Delphinium* alkaloids, has also been reported as a source of insecticidal material. McIndoo and Sievers,[46] who have already been mentioned, tested the insecticidal values of 232 preparations from 54 species of plants against a total of 28 species of insects. Drake and Spies,[50] and Spies,[51] tested a considerable number of plant extracts against goldfish. Further work may bring to light other promising insecticidal material from plant sources. The desirable properties of the substances already known, such as pyrethrum and rotenone, should stimulate such a search, although at present more emphasis seems to be placed on the search for synthetic organic compounds.

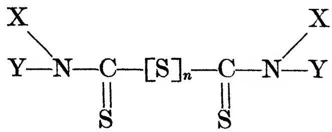
SYNTHETIC ORGANIC CONTACT INSECTICIDES

The work on synthetic organic compounds as stomach poisons, discussed previously, includes certain compounds which may function as contact insecticides as well. In general, the organic materials which have been tested as contact insecticides fall into two general classes: sulfur compounds, including the thiocyanates, and the amines.

Organic Sulfur Compounds. Roark and Busbey [52] have prepared a list of the organic sulfur compounds used as insecticides (exclusive of mothproofing materials). In this the authors list over 300 compounds, obviously too great a number for individual discussion here. Included in this list are the following classes of compounds: carbamates; thiuram derivatives; mercaptans; sulfides, aromatic and aliphatic, including carbon disulfide; oxygenated sulfur compounds, such as the sulfonic acids, sulfochlorides, sulfones, sulfoxides, sulfites and sulfates; sulfonamides, thiazine, and thiazole derivatives; thioacids, thiophenes, thioureas, and xanthates. Many of these compounds have been tested by Campbell et al,[53] Richardson and Smith,[54, 55] Tattersfield and Roberts,[56] and others.

Few of the synthetic organic sulfur compounds have found commercial application, other than the thiocyanates and carbon bisulfide, both of which will be discussed later.

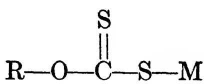
The thiuram sulfides which have the general formula



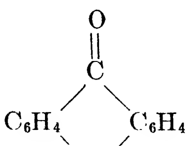
where *X* is an alkyl or aralkyl group, and *Y* is an alkyl, aralkyl, or aryl group, or where *X* and *Y* together form a methylene chain, and *n* is 1, 2, or 3, have been patented (B.P. 406,979) and are marketed as repellents against the Japanese beetle.

The thiazine and phenothiazine derivatives have been discussed under stomach poisons, although the question as to whether such materials act as contact or stomach poisons is not decided.

The alkali metal xanthates have also been patented (U. S. 1,716,273) for use as insecticides, and appear to hold some promise. The formula for these compounds is:



Here *M* may be Na, K, or Ca, or the radical of an organic base, etc., and *R* the radical of hydroxyl compounds obtained from the catalytic vapor oxidation of hydrocarbons. Emulsions of xanthated oils may be used as insecticides. Xanthone, a diphenylene ketone oxide,



is now available commercially as an insecticide.

The organic thiocyanates (rhodanates) were first suggested as insecticides by Murphy and Peet [57] who found an aliphatic thiocyanate (constitution unspecified) to be highly toxic to aphids. Such thiocyanates, containing one or more negative elements in the organic radical, and having the formula R–S–C–N, have been patented (U. S. 1,808,893). A 50 per cent solution of β-butoxy-β'-thiocyanodiethyl ether in kerosene is now sold as an insecticide.

Bousquet, Salzberg, and Dietz [58] investigated the combination of the long-chain fatty alcohols and the thiocyanate radical, and found that of those tested, the lauryl thiocyanate was the most effective against aphids. This material, $CH_3(CH_2)_{10}CH_2SCN$, is produced by the reaction of sodium thiocyanate and lauryl chloride. A material composed mainly of lauryl rhodanate (thiocyanate) and a wetting agent is being sold as a contact spray. This has many desirable properties as an insecticide, being relatively non-toxic to higher animals and plants at concentrations used to kill insects.

Hartzell and Wilcoxon [59] found that among 15 organic thiocyanogen compounds tested, the most satisfactory was thiocyanopropyl phenyl ether, considering both the insecticidal and phytocidal action of the materials.

The thiocyanates and certain other organic sulfur compounds have found considerable use as mothproofing agents. Alpha naphthyl isothiocyanate is said to be effective against houseflies, clothes moths, carpet beetles, etc., and is used in combination with pyrethrum.

The Amines and Related Compounds. The first work on the use of amines as contact insecticides was done by Tattersfield and Gimingham.[60] These authors studied the quaternary ammonium compounds and trimethylamine, the aromatic amines, the naphthylamine derivatives, and some N-heterocyclic compounds. Using *Aphis rumicis* as the test insect, they found that the tetramethyl ammonium hydrate and chloride were more toxic than the corresponding tetraethyl ammonium compounds. The aromatic amines, in general, were not highly toxic to aphids, and derivatives of α-naphthylamine were more toxic than the corresponding β-derivatives.

Among the heterocyclic compounds tested, the heterocyclic ring compounds constituting nicotine were much less toxic than nicotine itself. The order of toxicity of some of the simpler N-heterocyclic compounds was found to be: pyrrole $<$ pyridine $<$ picoline $<$ quinoline $<$ isoquinoline $<$ acridine. Finally, Tattersfield and Gimingham found that hydrogenation of pyridine and pyrrole to piperidine and pyrrolidine increased their toxicity. This substantiated the earlier findings of Richardson and Smith.[55] Benzyl-pyridine was the most toxic derivative of pyridine tested.

Studies on the cyclohexylamine derivatives have been reported by Kearns and co-workers; [61, 62, 63] in the first paper of this series 41–N and N–N substituted derivatives of cyclohexylamine were tested on the aphid *Myzus porosus* and the greenhouse red spider, *Tetranychus telarius L.* Two of the compounds tested, N, N-amyl-benzoyl cyclohexylamine and N, N-amyl-acetyl cyclohexylamine were found to have exceptionally high contact insecticidal properties.

Since the parent substance in these derivatives may be considered to be ammonia, Kearns and Flint [61] discussed the relation of toxicity to chemical constitution using this as a nucleus. Starting from the work of Tattersfield and Gimingham,[60] in which it was found that the substitution of one of the hydrogen atoms with a cyclohexyl group to form cyclohexylamine produces a compound with greater toxicity than the primary aliphatic or aromatic amine, Kearns and Flint tested a number of the N-substitution products and found that the substitution of the second hydrogen atom of NH_3 by an alkyl group tended to produce greater toxicity than various acyl, aryl, or aralkyl substitutions. It was further shown that the greater the number of carbon atoms in the alkyl group, the greater the toxicity at least up to and including the octyl derivatives, although the higher members of the series tend to become progressively less water-soluble.

The substitution of certain acyl groups for the third remaining hydrogen atom of NH_3 produced an exceptionally toxic compound, provided that the other two replaceable atoms were substituted by an alkyl group, such as amyl and the cyclohexyl group. There does, moreover, appear to be a specific relationship between the different substitution products, which these authors were not able to explain satisfactorily.

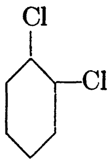
The two compounds mentioned previously; namely, the N, N-amyl-acetyl and N, N-amyl-benzoyl cyclohexylamines, were found [62] to be too injurious to apply to greenhouse plants at sufficient concentrations to kill the greenhouse red spider. A new derivative of cyclohexylamine, the N, N-amyl-benzyl product, was therefore tested and found non-toxic to plants at concentrations high enough to give satisfactory control of these insects.

In a recent paper on the subject, Kearns and Compton [63] describe N, N-amyl-benzyl cyclohexylamine, a compound more

active insecticidally and less toxic to plants than the N, N-amylbenzoyl derivative, although, as this compound is immiscible with water, the efficiency depended on the amount and kind of emulsifier used.

Miscellaneous Contact Insecticides. Hexachlorethane, C_2Cl_6, a solid, melting at 185° C., has been used as a mosquito control measure in France. This compound, which sublimes to some extent at ordinary temperatures and has an odor similar to camphor, is mixed with talc and the mixture ground to an impalpable powder. This powder is then blown on the surface of stagnant water in which the mosquito larvae are located. It is said to be non-toxic to man and higher animals.

Orthodichlorobenzene:



is used against the larvae of the crane fly in golf greens, and against certain powder post beetles (*Lyctus*). Mixed with glue it is said to protect cabinet work against wood boring insects.

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CHAPTER VII

SULFUR AND INORGANIC SULFUR COMPOUNDS

Sulfur and a number of its inorganic compounds function both as insecticides, as well as acaricides, and fungicides, and, although first used as insecticides, now are probably more widely used to destroy fungi. The chemistry of the sulfur derivatives will be considered at this point, however, since these compounds are among the most useful of insecticides.

A rough estimate indicates a world consumption in 1937 of 550,000,000 pounds of sulfur for use as insecticides and fungicides. Of this total, France accounted for 110,000,000 pounds, Italy 165,000,000 pounds, and the United States used approximately 45,000,000 pounds for dusting purposes and half that amount, about 22,000,000 pounds, as lime sulfur preparations. It has been estimated that about 23 per cent of the sulfur used in the United States was used as fertilizers, insecticides and fungicides.

Elemental Sulfur

Free sulfur in its native state occurs in deposits presumably of volcanic origin in many parts of the world. Sulfur occurs in a number of crystalline varieties, and in two distinct allotropic forms, called α- or rhombic and β- or monoclinic. The rhombic is the stable form at ordinary temperatures, and all other forms pass into rhombic sulfur on standing. The specific gravity of this form is 2.07, and the melting point 112.8° C. It is insoluble in water, slightly soluble in alcohol and ether, and freely soluble in carbon disulfide, sulfur chloride and hot benzene.

Sulfur for use as an insecticide and acaricide was originally sold as "flowers of sulfur," consisting of small crystals produced by sublimation. It was soon discovered, however, that more finely divided preparations were more effective, and at the present time sulfur sold for insecticidal or fungicidal use is ground to pass at least a 300-mesh sieve, and there is a distinct trend toward the use of extremely finely divided sulfur, particularly for spraying. Streeter and Rankin,[1] and Goodhue,[2] have published studies on the particle size of commercial sulfur for spraying purposes.

The "Micronized" sulfur, produced in a special air-grinding apparatus, has a mean particle diameter approaching that of the so-called colloidal sulfurs. Wilcoxon and McCallan [3] have shown that the toxicity of sulfur to conidia of *Sclerotina americana* is a function of the fineness of the particles. The adhesive properties of sulfur are also enhanced by finer division. Wilcoxon and McCallan [4] found that the adherence of sulfur particles to glass slides following a rain treatment depends on the degree of fineness of the dust, the smaller particles being most adherent. The adherence to leaves was in general greater than to glass and increased with the roughness and hairiness of the leaf surface. Streeter and Rankin [1] assumed that sulfur particles having a diameter greater than 27μ will fail to adhere to foliage for any length of time.

Goodhue,[2] using a new method of sedimentation, found that many of the ground sulfur samples examined (including the "conditioned" and "wettable" sulfurs commercially available) contained as much as 35 per cent of particles less than 10μ in diameter, whereas the sublimed "flowers" of sulfur were variable in particle size.

Sulfur, even though finely ground, is not wetted by water, so that the addition of a wetting agent is necessary for the preparation of aqueous suspensions for spraying purposes. Volck [5] suggested the use of flour for this purpose, and other materials have been recommended from time to time, including dextrins, calcium caseinate, glue, resins, skimmed milk, bentonite, sulfite liquor and, more recently, a variety of organic wetting agents (see later chapter).

White [6] has reported tests of the deposition and retention of sulfur on various plant surfaces, using in all, 16 combinations of amendments to increase the wetting and sticking of the sulfur. He found that deposits varied with the type of plant surface, and that it was impossible to generalize.

Conditioned sulfur is the term applied to dusting mixtures containing a material such as gypsum, bentonite, talc, etc., in small amounts to make the sulfur flow more freely.

MODIFIED FORMS OF SULFUR

By far the greater part of the sulfur used as insecticide and acaricide is in its natural state; that is, even though it may be

mixed with other materials, it is used in the form in which it was extracted from the earth. Certain other forms of sulfur have been used for insecticidal purposes which, although they are elemental sulfur, are produced by chemical reaction. Such forms have found favor either because of their fine state of division or because of some other desirable property, and may be called "colloidal" and "flotation" sulfurs.

"Colloidal" Sulfur. Young[7] and de Ong[8] first studied the preparation and properties of colloidal sulfur as an insecticide. Two forms of colloidal sulfur were prepared by de Ong, one a hydrophylic sol made by passing hydrogen sulfide through a saturated solution of sulfur dioxide in water:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

Preparations made in this manner were relatively stable, with the greater part of the sulfur remaining in true colloidal suspension for some time. This type of colloidal sulfur may also be prepared by the reaction of sodium thiosulfate and sulfuric or other mineral acid·

$$Na_2S_2O_3 + H_2SO_4 \rightarrow Na_2SO_4 + SO_2 + S + H_2O$$

Such hydrophylic sulfur sols are sometimes called Odén sols, after the Swedish investigator.[9]

Hydrophobic colloidal sulfur was prepared by de Ong by acidifying lime sulfur solution with hydrochloric or sulfuric acid. Such preparations are sometimes called "precipitated sulfur" or "milk of sulfur." This reaction apparently is as follows:

$$CaS_x + 2HCl \rightarrow CaCl_2 + H_2S + S_{x-1}$$

Such hydrophobic suspensions tend to aggregate and to precipitate after a few days, but may be stabilized with a fair degree of success by the addition of a hydrophylic colloid, such as glue, gelatin or other similar material.

The hydrophylic sulfur preparations were found by de Ong to have greater toxicity than the hydrophobic, possibly because of the difference in particle size. Tisdale[10] suggested the field use of colloidal sulfur prepared from $Na_2S_2O_3$.

At present there are a number of "colloidal" sulfurs on the market for insecticidal use, although not all of them are what the

name implies, and some are probably only extremely finely ground straight sulfur.

Flotation Sulfur. This form of sulfur is a by-product of the manufacture of fuel gas from coal. When bituminous coal is carbonized to produce coke and gas, the sulfur present in the coal is driven off as hydrogen sulfide, which must be removed from the gas. The removal is accomplished in a variety of ways, one of the most modern of which is the absorption of the hydrogen sulfide in an alkaline solution, which when oxidized in the presence of a suitable catalyst yields elemental sulfur in a very finely divided state. It is then recovered by a flotation process, from which the product is named. Flotation sulfur is in a fine state of division, the particles approaching colloidal dimensions. Goodhue [2] found in examining the particle size of two samples of paste flotation sulfur that 94 and 100 per cent, respectively, of the fine particles had particle diameters less than 10μ, while 80 and 45.5 per cent of the particles had diameters less than 4μ. Sauchelli [11] states that over 95 per cent of the particles of flotation sulfur paste are not over 3μ in diameter.

Flotation sulfur is marketed both as a paste and in the dry form, often with some material added to make it wettable. As produced, flotation sulfur contains impurities, such as hydrocyanic acid and thiosulfates which must be removed by washing. The mean particle size of the dried product is, as might be expected, slightly larger than that of the paste, but due to shipping costs and ease of handling, the dry form is more commonly used at present.

SULFUR COMPOUNDS

ALKALI SULFIDES AND POLYSULFIDES

One of the most important groups of compounds used as insecticides and fungicides includes the polysulfides of the alkali metals, including ammonium. As mentioned previously, these materials, although they were first used as acaricides and insecticides, are now more widely used as fungicides.

Lime Sulfur. When a suspension of calcium hydroxide is boiled with sulfur, reaction takes place resulting in the formation of a number of sulfides of calcium. Lodeman [12] cites a preparation recommended by Kerrick in 1833 for the destruction of a white,

mealy insect, the formula for which was:

Quicklime	½ peck
Flowers of sulfur	½ pound
Lampblack	¼ pound

The concoction was prepared by mixing these ingredients with boiling water, and it is quite possible that some sulfides of calcium were formed by this process. It was not until 1851, however, that one Grison, head gardener of the vegetable houses at Versailles, in France, boiled together equal parts of lime and sulfur and used the clear liquid resulting as a fungicide.[12] The solution thus became known as "Eau Grison," but apparently was forgotten as a plant spray for considerable time. A combination of lime and sulfur boiled together was used as a sheep-dip in California, apparently of Australian origin, and was used successfully as a spray against San José scale by F. Dusey in 1886. It was introduced in the eastern United States about 1900, and during the past 40 years its use has increased until the present; 43,000,000 pounds (dry basis) were used during 1936.[13]

The first preparations contained salt, although no reason for its presence is found in the literature, except that it served to elevate the boiling point of the solution. This ingredient was early found to be superfluous, and omitted.

Chemistry of Lime Sulfur. Probably more has been written concerning the chemical reactions of lime sulfur than any other spray material. Unfortunately, much of the work is contradictory, and considerable of the early work is definitely misleading. List,[14] Trumble [15] and more recently St. John and Groves [16] have summarized the literature on the subject, so that only the more important papers will be cited here.

When sulfur and calcium hydroxide are suspended in water together and heated, a series of physical and chemical changes take place. The ingredients react, the reaction products go into true solution, and at the same time the color of the solution passes from a light yellow through deeper shades of orange until it finally becomes a deep red-orange. It has been established that the products of the reaction include sulfides of calcium, calcium thiosulfate and water.

Tartar and Draves [17] found that when an aqueous solution of an alkali or alkaline earth hydroxide is allowed to react with

sulfur the composition of the product depends upon the following conditions:

1. Initial concentration of the hydroxide.
2. Duration of the reaction period.
3. Temperature of reaction.
4. Relative amounts of reactants.

In some of the older work, it was assumed that the reaction

$$3Ca(OH)_2 + 12S \rightarrow CaS_2O_3 + 2CaS_5 + 3H_2O$$

took place, although the ratio of calcium thiosulfate to the calcium pentasulfide is usually much less than 1 : 2. This was accounted for by assuming that the thiosulfate was reduced to elemental sulfur.

The reaction between sulfur and calcium hydroxide, rather than being a simple process, probably takes place in a number of steps. It has been suggested that the first reaction is that which takes place between water and sulfur:

$$3S + H_2O \rightleftharpoons 2H_2S + H_2SO_3$$

This reaction proceeds at an extremely slow rate, for, according to Liming,[18] only a trace of hydrogen sulfide was found when wet sulfur was heated to 110° C. in the dark for five months, although this author found sulfur dioxide produced in measurable quantities from sulfur kept at lower temperatures in the presence of oxygen for the same length of time.

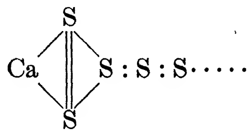
Martin,[19] in discussing the hydrolysis of sulfur, points out that in the presence of an alkali the reaction probably proceeds as follows:

$$2S + 4NaOH \rightarrow Na_2S + Na_2SO_2 + 2H_2O$$
$$(2S + 2HOH \rightarrow H_2S + H_2SO_2)$$

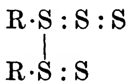
Unfortunately, there are no methods for the direct determination of the various calcium sulfides, and in fact the so-called polysulfides of calcium such as the tri-, tetra-, and pentasulfides have never been isolated,[16] the only assumption for their existence being the sulfur-calcium ratios of the products of the reaction. It is apparent from a study of these ratios that in most solutions of lime sulfur more sulfur is present than would be accounted for

by the existence of the monosulfide of calcium. The molecular ratio sulfur/calcium was found by Abbott, Culver, and Morgan [20] to average 4.68 in a series of 100 samples which they examined. Other workers have reported similar results, but whether calcium di-, tri-, quatra-, and pentasulfides exist as chemical compounds is open to question. Reckendorfer [21] has indicated that compounds or combinations of calcium with more than five sulfur atoms may exist in lime sulfur.

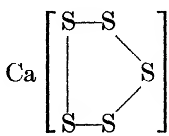
The chemical structure of the polysulfides has been investigated by a number of workers. Auld [22] has postulated the following structure for calcium pentasulfide:



while Thomas and Rule [23] have suggested the following configuration for the alkali polysulfides:



More recently Pearson and Robinson,[24] in a study of aqueous solutions of polysulfides, showed that the polysulfides as such exist in water solutions, and react as though they were combinations of a monsulfide plus additional sulfur, or according to the formula



In the light of certain other work, this type of representation is probably the most satisfactory. Such a representation would allow for the existence of compounds having 2, 3, 4, 5, or more sulfur atoms, depending upon the proportions of the reacting materials. Experimental work with the analysis of lime sulfur solutions further indicates that it is possible to titrate the so-called "monosulfide sulfur" separately from that making up the remainder of the molecule. The reader should be cautioned that according

to some writers "polysulfide sulfur" is taken to mean all of the sulfur combined with calcium as the sulfide, while others definitely state [17] that this fraction means that portion of the sulfide sulfur associated with the calcium *in excess of that required to form the monosulfide.*

It appears that from the point of view of insecticidal and fungicidal activity, the polysulfide sulfur is the most, if not the only, valuable constituent of lime sulfur solutions. Abbott, Culver, and Morgan [20] found that the calcium thiosulfates, sulfites and sulfates were without practical value against San José scale.

The older method of measuring the fungicidal and insecticidal value of lime sulfur preparations was by measuring the specific gravity, either in conventional units or according to the Baumé scale. Using this criterion, a preparation having a specific gravity of more than 1.283 (32° Baumé) is considered standard. Obviously, the presence of soluble materials, added unknowingly or as adulterants, will increase the specific gravity of the solution, and cases have been noted in which the specific gravity has been thus falsified. This has led to the practice, in some parts of the world, of selling lime sulfur solution on the basis of its polysulfide sulfur content. This would seem the most logical criterion by which to buy such material, although Thurston and Frear [25] have recently shown that with unadulterated lime sulfur solutions there exists a very high degree of correlation between specific gravity and polysulfide sulfur, so that buying on the basis of specific gravity is probably still satisfactory, particularly when the purchaser does not have the facilities available to make a chemical analysis. These authors further point out that most of the home-made samples of lime sulfur solutions examined by them were definitely deficient in polysulfide sulfur content, indicating that careful control of the manufacturing process is necessary for the production of a high quality product.

Reactions of Lime Sulfur. When lime sulfur solutions are boiled for a considerable period of time (91 hours according to Thompson and Whittier [26]) the calcium sulfides are completely broken down, with the formation of calcium thiosulfate and hydrogen sulfide. At one time it was thought that the reaction:

$$CaS_5 + 3H_2O \rightarrow CaS_2O_3 + 3H_2S$$

expressed this decomposition, but it was found that the amounts of thiosulfate formed did not correspond to this reaction. Thompson and Whittier found that after boiling for 23½ hours, both the thiosulfate sulfur and total calcium in solution began to decrease in amount. These authors believe that at this point the formation of calcium sulfite begins.

At temperatures below boiling, lime sulfur solutions also undergo decomposition, particularly when exposed to air. Simple dilution with water was found to decrease the amount of polysulfide sulfur present after one hour of stirring in the open air (Hodgkiss, Frear and Worthley [27]) from 93.87 per cent at 1–50 dilution to 93.50 per cent at 1–100 dilutions, and 92.50 per cent at 1–200 dilution,[28] although in solutions more concentrated than 1–50, the amounts of polysulfide sulfur were constant. This would appear to indicate that hydrolysis of the polysulfides takes place in dilute solutions.

It was further found by the same workers that raising the temperature of the solution from 23° C. to 32° C. greatly increased the decomposition of the polysulfide sulfur, with a corresponding increase in thiosulfate sulfur.

The continued stirring of dilute (1–50) lime sulfur solutions was found to hasten the decomposition, so that at the end of 45 hours, at 23° C., only 11.10 grams of sulfide sulfur were left per 100 gallons of the original 2106.80 grams per 100 gallons after one hour of stirring. The loss of sulfur as hydrogen sulfide was much too small to account for the sulfide sulfur lost, but the increase in thiosulfate sulfur was correlated to the decomposition of the sulfide. Approximately one-third of the total sulfur present in solution was precipitated as free sulfur at the end of 45 hours. The small amounts of hydrogen sulfide evolved led the authors to believe that the reaction was primarily one of oxidation. The amounts of the various constituents present after stirring at 23° C. are shown in figure 14.

Thompson and Whittier [26] found that passing either air or carbon dioxide-free air through concentrated solutions of lime sulfur for 21 days completely decomposed the sulfide sulfur present, although the solution through which air was bubbled contained approximately one-third of its sulfide sulfur after 14 days. The removal of carbon dioxide from the air which was bubbled through

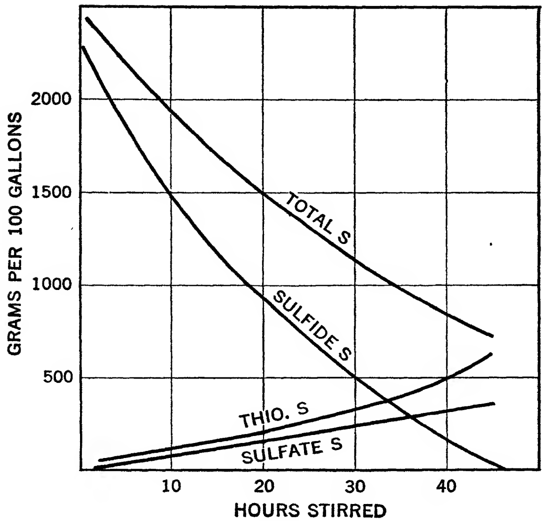


FIG. 14. Effect of time of stirring on the composition of liquid lime sulfur diluted 1–50 at 23° C. (From Hodgkiss.)

the solution had no effect on the speed or the extent of the decomposition.

The following reactions, then, express in a general way the oxidation process which takes place when lime sulfur solution is exposed to air:

$$CaS : S_x + 3O \rightarrow CaS_2O_3 + S_{x-1}$$
$$CaS_2O_3 \rightarrow CaSO_3 + S$$
$$CaSO_3 + O \rightarrow CaSO_4$$

so that, if one considers these three reactions, as well as the reaction of the polysulfides to give free hydrogen sulfide mentioned previously, a general picture of the decomposition of lime sulfur solution may be obtained. It should be emphasized that there are probably other reactions as well as the four mentioned taking place in the decomposition of lime sulfur solution, and no one reaction can be said to be wholly correct.

Reactions of Lime Sulfur with Other Spray Ingredients. The reactions taking place between lime sulfur and lead arsenate have been discussed on pp. 25–29, and will not be discussed further here. Since lead arsenate is the most common material combined with lime sulfur solution, a great deal of work has been done on the

chemistry of this combination, and little on other possible spray combinations based on lime sulfur. Andrew and Garman,[29] however, state that there is a negligible action between nicotine sulfate and lime sulfur when mixed in a spray solution, although there was a color change.

It has been known for some time that occasional severe injury occurs when sulfur sprays are followed closely by petroleum oil sprays applied to plants in foliage. But it appears that as a dormant spray the combination may be safe to use under certain conditions. No work of a chemical nature has been reported on this subject, apparently.

A spreader is sometimes used with lime sulfur solutions to increase the efficiency of the spray. Goodwin and Martin[30] found that the presence of a spreader caused an amorphous precipitate of lime sulfur to be deposited on the leaves, probably resulting in greater adherence. These same authors and Smith[31] have shown that calcium caseinate is not a suitable spreader, because the excess lime present may cause a reduction in the amount of sulfur deposited, and may cause injury to the plant. Ordinary soaps are also useless as supplement, since the insoluble calcium soaps are formed by reaction with the lime sulfur.

The use of ferrous sulfate as a supplement to lime sulfur solution was first suggested by Volck.[32] It has been found that this material not only increases adherece, but reduces injury to the plant as well. Apparently the mechanism of this reaction has not been investigated.

Manganese sulfate has been used in connection with lime sulfur in sprays as a corrective. The action of this material seems to result in the precipitation of colloidal sulfur which, as has been shown, is less likely to cause injury to the plants, although probably sacrificing some insecticidal and fungicidal efficiency at the same time.

Goodwin and Martin[33] have investigated the reactions between lime sulfur and calcium arsenate, and found that the soluble arsenic of calcium arsenate was reduced by the addition of lime sulfur solution.

Dry Lime Sulfur. The obvious economic advantages of a dry material over a liquid have led to the development of a dry lime sulfur preparation, which first appeared about 1917 (U. S.

Patent 1,254,908, reissued 14,870). A number of other patents have been issued: (see Abbott, Culver and Morgan[20]). This material is prepared by the evaporation of lime sulfur concentrate usually with sucrose as a stabilizer, and has been found by Abbott, Culver, and Morgan[20] to be considerably less effective against San José scale than the liquid preparation. These authors found an average of 64.90 per cent calcium polysulfides, 8.34 per cent calcium thiosulfate, and 9.86 per cent free sulfur in a series of samples examined by them. They further found that during the drying process the polysulfides apparently originally present as the tetra- and pentasulfides, with the latter predominating, were replaced by a mixture of the tri- and tetrasulfides in approximately equal proportions, a fact which, in the opinion of these authors, explains the decreased effectiveness.

Self-boiled Lime Sulfur. This form of lime sulfur solution, as the name implies, is produced without the use of external heat, the temperature rise of the solution caused by the slaking of calcium oxide being utilized to accelerate the reaction between the calcium hydroxide produced from this reaction with the sulfur present in suspension. This process was first described by Scott[34] in 1908, who used 15 pounds calcium oxide and 10 pounds of flowers of sulfur to 50 gallons of water. Only a small portion of the sulfur is chemically combined with the calcium by this process and large amounts of sediment are present. Self-boiled lime sulfur has been used mainly for sensitive plants, particularly on peach trees. It is only rarely used at present.

Dry Mix Sulfur-lime. This combination, also called "New Jersey dry mix," was proposed by Farley[35] in 1923 as a substitute for self-boiled lime sulfur for use on plants susceptible to injury. The original formula was:

Sulfur	8 pounds
Hydrated lime	4 pounds
Calcium caseinate	4 ounces

The mixture was considerably easier to prepare than self-boiled lime sulfur, and was rather widely used at one time, although the wettable sulfurs now available have largely replaced it in common use. Apparently there was no chemical reaction between the components, although Ginsburg[35] found that the calcium

hydroxide was readily carbonated on exposure to air, resulting in the formation of soluble arsenic when the dry-mix was used with lead arsenate.

Calcium Monosulfide.—CaS. This material was first suggested as a spray material by Hurt and Schneiderhan [36] in 1929. These workers used a mixture containing between 60 and 65 per cent of calcium monosulfide, and in addition, calcium sulfate, starch, and charcoal or coal in varying amounts. These impurities are normally present in the commercial grades of calcium monosulfide as a result of the process of manufacture by the reduction of anhydrous calcium sulfate with charcoal, coal, or starch at a temperature of 1000° C. The fungicidal value of the material was found to depend on the amount of calcium sulfide present, so that in the mixture this was considered to be the active principle.

Crude calcium monosulfide as used by Hurt and Schneiderhan was a powder, varying in color from pale gray to yellow, sometimes appearing darker when powdered coal was used as a reducing agent in the manufacture. It went into solution readily, has better adhering properties than sulfur-lime dry-mix and did not undergo decomposition on storage.

In three year trials on apples and peaches, good control of apple scab (*Venturia inaequalis* Cook, Winter), peach scab (*Cladosporium carpophilum* Thum.) and brown rot (*Sclerotinia cinerea* (Bon. Schrot.)) was obtained by the use of a spray of calcium monosulfide. Calcium monosulfide was found by Hamilton [37] to be relatively ineffectual in controlling severe infestations of apple scab in New York. Calcium monosulfide has never been widely used, being replaced, as have many other of the milder acting sulfur compounds, by the wettable sulfurs.

Ammonium Polysulfide. This material, apparently similar in chemical constitution to lime sulfur, is prepared by passing hydrogen sulfide into concentrated ammonium hydroxide (28 per cent) to saturation and then dissolving an excess of sulfur in the resulting solution of ammonium sulfide. Although this material has long been used as a reagent in chemical analyses, Eyre and Salmon [38] first used it as a spray in 1916 against the gooseberry mildew (*Sphaerotheca mors-uvae* (Schw. Berk.)). Little is known of the chemistry of ammonium polysulfide (sometimes referred to as A. P. S.), except that due to the absence of air during the manu-

facturing process less sulfur is present as the thiosulfate and sulfate than in lime sulfur.[39] Ammonium polysulfide is apparently less stable than the calcium salt, and due to the volatility of the ammonium radical more free sulfur is deposited on decomposition. Recently Compton and Kearns [40] have used ammonium polysulfide as a greenhouse spray against red spider with considerable success, although the fumes evolved were toxic to certain species of plants. It is not widely used in this country.

Potassium-ammonium-seleno-sulfide.—$(KNH_4S)_5Se$. While this material probably depends for its toxic action more on the presence of selenium than on the sulfur, it is grouped with the sulfides because of the similarity of action. Compton and Kearns [40] found it to be very efficient in controlling red spider on greenhouse crops when applied at 2 per cent concentration (the material on the market contains 8 per cent of potassium-ammonium-seleno-sulfide). When diluted with water, observation shows that a large part, if not all, of the selenium is liberated as finely divided, dark red particles of the element. The presence of selenium, a highly toxic element, would indicate a rather limited usefulness as a spray material, although Hoskins, Boyce, and Lamiman [41] found no health hazard when the compound was used moderately.

Potassium and Sodium Sulfides. The sulfides of potassium, liver of sulfur, and sodium have long been used as fungicides and insecticides, either as a solution of the salts alone or as a homemade preparation. This is prepared by boiling sulfur and an alkali hydroxide together in a manner similar to the preparation of lime sulfur solutions, although the reaction between sodium and potassium hydroxides and sulfur will proceed without the addition of heat. Such a preparation of sodium hydroxide (lye) and sulfur is described by Lodeman [12] and Haywood.[42]

The active principles of such mixtures appear to be the alkali mono- and polysulfides, and their chemistry is similar to that of lime sulfur, but, because of their infrequent use, little has been done to investigate the chemistry of these materials. It is known, however, that, like lime sulfur solution, these solutions are readily decomposed in the presence of oxygen. Haywood [42] reports that, in a sodium sulfide solution prepared by him, 18 per cent of the total sulfur was present as sodium thiosulfate, the balance as "polysulfides and sulfides." Goodwin, Martin, and Salmon [43]

analyzed several samples of sodium sulfide solutions and found that the monosulfide content varied from 0.60 to 4.32 per cent or from 11.2 to 20.5 per cent of the total sulfur present; the polysulfide sulfur from 4.16 to 11.82 per cent or from 55.4 to 77.5 per cent of the total sulfur present; and the thiosulfate sulfur from 0.32 to 5.18 per cent, or from 4.7 to 25.0 per cent of the total sulfur present. Sulfates and sulfites are also formed during the process of manufacture, and on exposure to air. The sodium sulfate, unlike the corresponding calcium salt, is soluble and therefore remains intimately mixed with the active constituents. Possibly for this reason, as well as for the fact that the sodium and potassium hydroxides are more caustic than calcium hydroxide, the sulfides of the former elements have never been as widely used as lime sulfur, and at present are rarely used as sprays. Abbott, Culver, and Morgan [20] tested a dried preparation of "sodium sulfur" and found that, while it gave results similar to dried lime sulfur, it was not particularly effective against San José scale.

Barium Sulfides. Goodwin, Martin, and Salmon [43] tested a preparation made by saturating barium hydroxide solution with hydrogen sulfide, and found that the greater part of the sulfur was present as the polysulfides, with some as the thiosulfate, monosulfide, and sulfate. Although this solution was found to be fungicidal it apparently offered no advantages over lime sulfur solution. Abbott, Culver, and Morgan [20] also tested a dried "barium sulfur" compound, and found it less effective than liquid lime sulfur. This material has never come into common use.

MISCELLANEOUS SULFUR COMPOUNDS

Sulfur Nitride—S_2N_4. Recently, Fulton [44] has suggested sulfur nitride as a possible insecticide and fungicide. Made from ammonia and sulfur chloride according to the reaction:

$$16NH_3 + 6S_2Cl_2 \rightarrow 12NH_4Cl + S_2N_4 + 8S$$

(U. S. patent 2,101,645).

Sulfur nitride occurs in orange red monoclinic crystals. It has not yet been tried to any extent as an insecticide and fungicide.

MECHANISM OF THE TOXIC ACTION OF SULFUR

Although the toxicological action of insecticides and fungicides is considered to lie outside the province of this text, a brief discus-

sion of the theories relating to the toxic action of sulfur will be given, because of the chemical considerations involved.

Considerable evidence exists to indicate that sulfur may act on living organisms at a distance. The early workers on the subject considered that either (1) sulfur vapor or (2) sulfur dioxide was responsible for this action. More recently it has been suggested that the toxic action is due rather to (3) pentathionic acid or (4) hydrogen sulfide. Each of these suggestions will be discussed in some detail.

Sulfur Vapor (Volatilized Sulfur). The work of Tucker [45] has shown that sulfur, even when at the relatively low temperatures prevailing outdoors during the summer in the temperate zone, is volatilized, and, under suitable conditions, may be condensed. Liming [18] has studied the rate of this volatilization, and found that the relative rates of volatilization at various temperatures were as follows: 24° C., 1.0; 30° C., 5.1; 35° C., 10.2; 50° C., 79.0; 70° C., 1,304.0; 93° C., 19,560.0. It is to be noted that over the ordinary range of atmospheric temperature included in this study, up to 35° C., the increase in rate of volatilization was relatively small: from 1 to 10. Nevertheless, volatilization did occur at an appreciable rate at these temperatures. Light and humidity apparently did not influence the speed of volatilization. This agreed with the work of Goodwin and Martin.[46] The speed of volatilization was greater with finely divided crystalline sulfur particles than with coarser, amorphous particles.

Regarding the toxicity of sulfur vapor, however, there seems to be some divergence of opinion. Liming [18] found volatilized sulfur to be without effect on the germination of fungus spores, a result in agreement with the report of Goodwin and Martin [47] that no toxic action of sulfur vapor was observed against the fungi *Erysiphe graminis* and *Sphaerotheca humuli*. These authors did find, nevertheless, that volatilized sulfur was toxic to the gall mite *Eriophyes ribia*, a mite relatively tolerant to sulfur dioxide and hydrogen sulfide.

From this work it would appear that sulfur in appreciable quantities is volatilized at atmospheric temperatures and, though the volatilized sulfur is without great toxicity to fungus spores and hyphae, it may be toxic to certain animate organisms.

Sulfur Dioxide. Recent work has in general failed to support the contention that sulfur dioxide (SO_2) plays any important part in the toxic action of sulfur at a distance. Liming [18] found that some sulfur was oxidized to sulfur dioxide at ordinary room temperatures, but the quantities were small. This author, in testing the toxicity of sulfur dioxide, concluded that gaseous sulfur dioxide was not highly toxic to the spores of *Sclerotinia cinerea*, although the data presented indicate that germination was prevented completely at relatively low concentrations if sufficient exposure were given. Water solutions of the gas at the higher concentrations inhibited spore germination. Goodwin and Martin found sulfur dioxide to be only slightly toxic to mites.

Pentathionic Acid. This compound, formed by the oxidation of sulfur, was suggested by Young [7] as the toxic factor in sulfur fungicides. According to Williams and Young,[48] it is formed as follows:

$$S + O_2 \rightarrow SO_2$$
$$SO_2 + H_2O \rightarrow H_2SO_3$$
$$H_2SO_3 + S \rightarrow H_2S_2O_3$$
$$5H_2S_2O_3 \rightarrow 2H_2S_5O_6 + 3H_2O$$

These authors indicated that the acidity of sulfur dusts was due to pentathionic and sulfuric acids, and that the pentathionic acid was responsible for the toxic action. A series of papers by Young and co-workers, and by Liming,[18, 49, 50] advanced this theory. Liming [50] prepared pentathionic acid and sodium, barium, and potassium pentathionates, and found the acid to be toxic to a number of species of pathogenic fungi, bacteria, and insects (aphids).

This work has been challenged by several workers, principally Wilcoxon and McCallan,[3] and Roach and Glynne,[51] the former finding, in a study which may well be taken as a model for this type of investigation, that the toxicity of pentathionic and sulfuric acids was the same, and was apparently due to the hydrogen ion concentration, a comparatively high concentration of which was required. The neutral salts of pentathionic acid were also found to be non-toxic to conidia of *Sclerotinia americana*. As a final proof, since Young had stated that the toxicity of sulfur dust was in proportion to the pentathionic acid present, Wilcoxon and

McCallan tested two samples of dusting sulfur, identical except that one had been treated with sodium hydroxide to remove pentathionic and sulfuric acids, while the other was untreated. Both samples showed the same toxicity.

It appears, then, that while certain polythionic acids, notably pentathionic acid, are present in small amounts in finely divided sulfur, its presence is not a factor of importance in the fungicidal, and presumably the insecticidal, action of sulfur.

Hydrogen Sulfide. Barker [52] and Marsh [53] first called attention to the fact that hydrogen sulfide was formed when sulfur was dusted on living leaves or on fungus colonies or mixed with fungus spores. Liming,[18] in supporting the pentathionic acid theory, found that hydrogen sulfide was not formed from sulfur in the presence of light and moisture except at relatively high temperature. He did, however, confirm the fact that hydrogen sulfide was formed from sulfur by the action of fungus colonies (*Sclerotinia cinerea*), but claimed that pentathionic acid present in the sulfur applied was responsible for the toxicity.

About the time the pentathionic acid theory of toxicity was being promoted by Young et al., Wilcoxon and McCallan,[3] as mentioned previously, presented the results of an extensive investigation on the subject of the mechanism of sulfur toxicity. Briefly, these authors found that hydrogen sulfide was from 6 to 200 times as toxic to the fungi tested as pentathionic and sulfuric acids, which were approximately equal in toxicity.

McCallan and Wilcoxon [54] in a later paper thoroughly investigated the production of hydrogen sulfide from sulfur and its toxic action and found that (1) all species of plants tested were found to evolve hydrogen sulfide when in association with sulfur; (2) actual contact between the sulfur and the plant material was not necessary for the production of hydrogen sulfide; (3) the production of hydrogen sulfide under the conditions given above seemed to have an optimum at 35° C., was inhibited entirely at 60° C., and seemingly is an enzymatic reaction; (4) hydrogen sulfide was highly toxic to the fungus spores tested, the toxicity varying with different species. Finally these workers postulated that sulfur vapor, known to be given off by elemental sulfur at ordinary temperatures, from the sulfur particles is reduced within the spores or other plant cells to form toxic hydrogen sulfide.

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CHAPTER VIII

THE OILS

Petroleum Oils and Their Classification

According to origin, crude petroleum oils are usually classified as paraffinic or naphthenic (asphaltic). Crude oils from the Pennsylvania region are rich in saturated hydrocarbons (paraffins), while Mid-Continent, Mexican, and Gulf Coast oils contain increasing amounts of aromatic and polymethylene compounds (naphthenes), with larger amounts of sulfur compounds.

Inasmuch as practically all petroleum oil for insecticidal use has been subjected to separation and purification processes of one kind or another, usually distillation, further classification is necessary. At the present time the distilled fractions from crude petroleum are, in the order of volatility, casinghead gasoline, gasoline, kerosene, gas oils, and light lubricating (neutral) oils. From the residues of the distillation, most of the lubricating oils ("bright stock") are derived, as well as the solid fractions, petrolatum, and paraffin wax (from the paraffinic crudes), or petroleum pitch or asphalt (from the asphaltic crudes).

In general, the process of distillation separates the various fractions according to molecular weight and viscosity, the higher boiling fractions being composed of larger molecules and having greater viscosity. Specifications for the various fractions usually include the boiling range, specific gravity and viscosity. The kerosenes, for example, are those oils with boiling points between 150° C. and 300° C. and a specific gravity of from 0.76 to 0.85.

The viscosity of an oil has great influence on its insecticidal effectiveness, and is usually measured by determining the time necessary for a given volume of oil at a definite temperature to flow through an orifice. In the Saybolt viscosimeter the volume of oil taken is 60 ml., the temperature 100° F. (37.8° C.), and oil viscosity is usually expressed as Saybolt viscosity (seconds) or as absolute viscosity (poises) at some specified temperature.

After distillation, the various fractions of the oil are refined, the degree of refinement depending upon the intended use of the

oil. Certain unsaturated compounds may be present in the original crude oil, and some may be formed during the distillation process. These are removed by treating the distillate with sulfuric acid or sulfur dioxide, thus sulfonating the unsaturated compounds, which are then removed. This process for removing the unsaturated hydrocarbons is not to be confused with a similar treatment (Edeleanu process) for removing sulfur compounds. Liquid paraffin, sometimes called Russian mineral oil, white oil or "Nujol" is prepared by a similar but more drastic sulfonation process. Oils of this type are used as sprays for certain purposes.

OILS USED AS INSECTICIDES

Petroleum oils apparently were first mentioned as insecticides by Goeze [1] in 1787. It was not until about 1865, however, that a petroleum distillate, kerosene, was first used against scale insects on orange trees.[2] Other petroleum preparations have been used quite extensively, particularly as dormant sprays.

Crude Oil. As a spray, crude oil was apparently first used by Smith [3] in 1897, who applied a 25 per cent emulsion of the oil both as a dormant and a summer spray. The oil was emulsified with soap, a hot soap solution being mechanically mixed with the oil. Later, "miscible oils" appeared, in which the emulsifier was dissolved in the oil with the aid of phenol, cresylic acid, or naphthalene. These had the obvious advantage of being concentrated and were easily diluted to the required strength for application. Nevertheless, the variability of crude oils made difficult their use, and impurities present often caused severe damage to plants. This led to their replacement by the more refined lubricating oils.

Kerosene. Kerosene, although it was used alone as early as 1865, was first employed in the form of an emulsion with soap by Cook [4] in 1877. Other materials, such as sour milk, condensed milk, resin, clays, Bordeaux mixture, and many others have been used as emulsifiers. These will be discussed in more detail later.

The low boiling fractions of kerosene, probably because of their low viscosity and high volatility, have been found by Moore and Graham [5] to be less effective than the higher boiling fractions as emulsions, and have largely been replaced in common usage by the more viscous, less volatile oils.

It is believed that, as ordinarily prepared, kerosene is composed mainly of paraffin hydrocarbons with from 10 to 16 carbon atoms. The viscosity of kerosene is relatively low, too low to be measured accurately by the Saybolt viscosimeter, which usually is not employed for liquids with less than 32 seconds flow time.

Kerosene, as has been mentioned previously, is widely used as a solvent for pyrethrins, and kerosene solutions of these insecticides form the basis for most of the household insect sprays.

"Light and Medium" Oils. During the past few years it has become the custom to apply in the field oil sprays of greater viscosity and lower volatility than kerosene. Classification of these oils is difficult, since they are usually graded on differences in viscosity and specific gravity. Oils for summer spraying are usually classified as "light," and range in viscosity between 40 and 65 seconds Saybolt. These oils are highly refined, and contain more than 90 per cent unsulfonatable residue; in other words, they are composed almost entirely of saturated hydrocarbons, presumably made up from 14 to 18 carbon atoms per molecule.

The so-called "medium" oils have characteristics similar to the "light" oils, but are more viscous, from 65 to 85 seconds Saybolt. These oils are also highly refined, and contain but small amounts of unsaturated hydrocarbons. Both the "light" and "medium" oils are applied as emulsions, and are usually emulsified by the user.

"Heavy" Oils. Oils having a viscosity greater than 85 seconds Saybolt are usually classified as "heavy," and are used for insecticidal purposes principally as dormant sprays. For this purpose the oils need not be so highly refined, because danger of plant injury is much less under such conditions, and in many cases oil intended for lubricating purposes has been used successfully. These oils are also applied as emulsions, usually made by diluting a stock emulsion containing up to 85 per cent oil. For the control of certain insects other materials, such as dinitro-o-cyclohexylphenol (2, 4, dinitro-6-cyclohexylphenol), are added to increase the toxicity of the dormant spray, and thus allow a reduction in oil deposit and still maintain a satisfactory insect control. Such mixtures have been studied by Kagy and Richardson,[6] Dutton,[7] Hartzell and Moore.[8] Boyce et al.[9, 10] have recently made an extensive study of the properties of dinitro-o-cyclohexylphenol, par-

ticularly in relation to its use in this connection. Combinations of petroleum and tar oils are also widely used as dormant sprays.

CHEMICAL FACTORS AFFECTING THE USE OF PETROLEUM OILS AS INSECTICIDES

Most of the research on petroleum oils as insecticides prior to about 1930 was concerned with the use of this material as sprays on trees and shrubs. For this purpose two general types of oils were used: Relatively viscous and unrefined oils for dormant spraying, and lighter, more highly refined oils for foliage sprays. During recent years, however, the petroleum oils have found wider application, particularly as agents to assist in the more efficient application of other insecticidal materials, as in the case of pyrethrum- and rotenone-bearing sprays, inverted emulsions, "deposit builders," etc. Such preparations are described in some detail elsewhere.

The chemical reactions of the petroleum oils when used as insecticides have not been investigated as thoroughly as their importance warrants. The early work of Gray and de Ong [11] indicated that the degree of plant injury caused by an oil could be estimated with considerable accuracy by means of the sulfonation test (for a description of this test see Chapter XIV). In this test, the unsaturated aliphatic and aromatic hydrocarbons react chemically with sulfuric acid, while the saturated hydrocarbons do not. The latter comprise the unsulfonatable residue (U. R.). The higher the unsulfonatable residue percentage in an oil, the less likely it is to produce plant injury. Although this test is widely used, the mechanism of the phytocidal action was not clear until Tucker [12] pointed out that the hydrocarbons of spray oils have little toxic action on plant leaves until they are oxidized to oil-soluble acids. Saturated hydrocarbons apparently do not oxidize under normal conditions with sufficient rapidity to cause plant injury, but the unsaturated hydrocarbons under the influence of light, particularly ultra-violet radiation, rapidly absorb oxygen and thus become increasingly dangerous. The exact mechanism of this reaction is not thoroughly understood, but it appears that peroxides are first formed which are later oxidized to acids. Fenske et al.[13] have estimated that these acids contain one carboxyl group in a

molecule having a molecular weight of approximately 1500. In addition to the direct effect of these acids upon the plant tissues, their presence is equally undesirable in oil mixtures containing dissolved or suspended insecticidal material such as the pyrethrins which may be subject to decomposition.

Because this decomposition of oils is of great importance in industrial lubrication, transformer insulation, and the like, many workers have sought means of preventing it. Strangely enough, highly refined oils may develop greater acidity than less refined oils exposed under similar conditions. This difference seems to be due to the presence of natural antioxidants in the cruder grades of petroleum oils which are removed during the refining process. For industrial use, a group of synthetic antioxidants has been suggested, including phenolic derivatives, amines, and such sulfur compounds as disulfides and thioethers. The literature does not contain references to the use of such materials in spray oils, but it would seem that they might be of assistance here.

Even though the use of oil-sulfur combination sprays often causes severe foliage injury, Hoskins [14] reported that the addition to the oil of free sulfur or sulfur in such combinations as hydrogen sulfide, organic sulfides, disulfides, and mercaptans did not increase the oxidation of the oils used. The addition of sulfur in any of these forms did, however, result in severe leaf injury. It has been found by a number of workers that both transpiration and photosynthesis in oil-sprayed plants were below normal.[15, 16]

VEGETABLE AND ANIMAL OILS AND THEIR DERIVATIVES

Oils of vegetable and animal origin were early found to possess insecticidal properties, and, because of their availability, were widely used, particularly after saponification. As soaps will be considered in a later section, only the oils themselves will be discussed here.

Chemistry of Vegetable and Animal Oils. The terms *fat* and *oil* as applied to substances of animal and vegetable origin are interchangeable, although a fat is usually considered to be solid at ordinary temperatures, while an oil is liquid. Chemically all such naturally occurring fats and oils are esters, or organic salts of the trihydric alcohol glycerine, and fatty acids. Because the glycerine

molecule contains three hydroxyl groups, it is possible to have a molecule of fat in which there are one, two, or three different fatty acids.

A wide variety of fatty acids have been found to occur in natural fats, and the characteristics of the fatty acid molecule composing the fat determine to a large extent the properties of that fat. With the exception of margaric acid, all naturally occurring fatty acids are composed of even numbers of carbon atoms, although they may be either completely saturated (formula $C_nH_{2n}O_2$) or unsaturated (formula $C_nH_{2n-2u}O_2$) where u equals the number of double bonds. All even-numbered members of the saturated series of fatty acids from C_2 to C_{30} have been found in biological material, but unsaturated acids with less than 18 carbon atoms occur only rarely.

Vegetable and animal oils differ from the petroleum oils in that they are less stable, being hydrolyzable without difficulty in the presence of acid, and forming soaps in the presence of alkali.

Vegetable Oils. As insecticides, vegetable oils are not often used in this country, because of the availability of cheap petroleum and tar oils which are generally more effective insecticides. Staniland [17] tested castor, sesame, cotton-seed, linseed, olive, and rape oils as sprays, and found that the rapeseed oil was the most satisfactory as an insecticide, killing certain insects at a concentration of 0.5 per cent. This investigator used the oil emulsions both at the "pink" stage and as summer sprays on apples. Rape (Colza) oil is secured from the seeds of several varieties of *Brassica Campestris*, of the order Cruciferae, cultivated extensively in Europe and Asia. The oil contains esters of rapic and erucic acids, as well as acids of the linolic and linolenic series. Rape oil stands between the drying and non-drying oils; in other words, the presence of unsaturated fatty acids permits combination with oxygen to a limited extent, although the oil does not form a "varnish" on oxidation as does linseed oil. Sulfur is present in the cruder grades of rapeseed oil, which may account in a measure for its effectiveness as an insecticide.

Other vegetable oils have been used by Austin, Jary, and Martin [18] and Balakhovskii [19] as insecticides. The former found that, while the vegetable oils were fairly efficient ovicides, their cost was prohibitive when compared with the petroleum and tar oils.

Animal Oils. The animal oils as such seldom have been used as insecticides. Certain of the fish oils have, however, found use as adhesives, and will be discussed under a separate heading. Fish and whale oil soaps are rather commonly used as emulsifying and wetting agents.

Fatty Acids. The component fatty acids making up the oil molecules are known to possess insecticidal value. These fatty acids are secured by the hydrolysis of fats according to the reaction:

$$
\begin{array}{lcll}
H_2C\text{—O—CO—R} & & H_2C\text{—OH} & \\
\quad | & & \quad | & \\
HC\text{—O—CO—R} + 3HOH & \rightleftharpoons & HC\text{—OH} & + \; 3HO\text{—CO—R} \\
\quad | & & \quad | & \\
H_2C\text{—O—CO—R} & & H_2C\text{—OH} & \\
\quad \text{Neutral fat} & & \text{Glycerine} & \quad \text{Fatty acid}
\end{array}
$$

The fatty acids produced by the hydrolysis of animal or vegetable fats are extremely varied in chemical composition, as has been already mentioned, although in general they are all straight-chain compounds and contain only carbon, hydrogen, and oxygen. The work dealing with fatty acids has been of more theoretical than practical importance, although the knowledge as to the relationships between chemical constitution and toxicity resulting from such studies is of considerable importance.

Siegler and Popenoe [20, 21] tested a number of fatty acids as contact sprays against insects, particularly aphids. They found that the toxicity of the fatty acids increases with the molecular weight, at least up to a certain point (about C_{10}), and that the free acids were more toxic than their corresponding soluble neutral or alkaline salts. In further tests against aphids, a preparation of long-chain fatty acids derived from coconut oil was found to be highly toxic at a concentration of 1 to 800–1200 parts of water. The acids present in this mixture were said to be mostly caprylic, capric, lauric, myristic, palmitic, oleic, and stearic.

Tattersfield and Gimingham [22] and Dills and Menusan [23] have also determined the toxicity of fatty acids, and found that the most toxic acids were those containing 10 to 12 carbon atoms, with toxicity to insects increasing with molecular weight up to this point and decreasing markedly with molecules having more than 12 carbon atoms. The findings of Dills and Menusan are shown in

figure 15. These authors found that the order of phytocidal activity in these fatty acids was the same as their insecticidal toxicity.

Soaps. Soaps, being readily available, were probably early used as insecticides, although Goeze [1] in 1787 appears to have been the first author to publish recommendations for their use in this connection. Among the soaps which were widely used as insecticides at an early date, the most important were those made from animal fats, particularly whale and fish oil soaps.

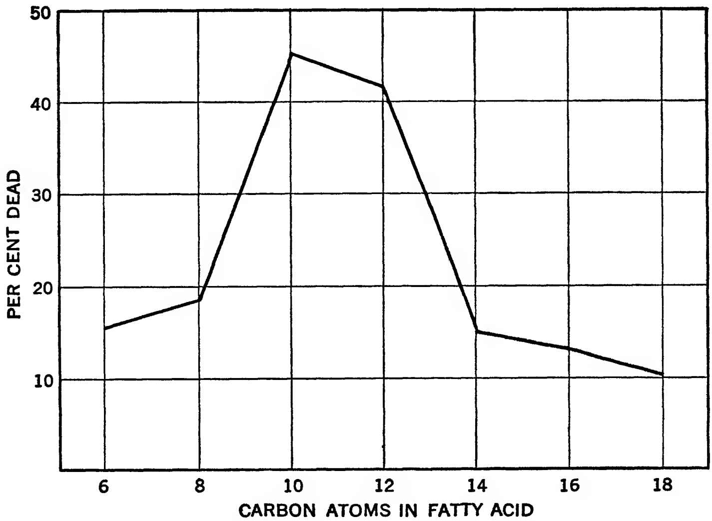

FIG. 15. Toxicity of one-sixth per cent fatty acids to *Aphis rumicis*. (From Dills and Menusan.)

Chemistry of Soaps. Soaps are defined as alkali salts of fatty acids, and are most commonly sodium salts (hard soaps) or potassium salts (soft soaps). Soaps are hydrolyzed to some extent, the process being similar to that observed in inorganic salts of a weak acid and a strong base, and increases with increased dilution. The reaction is

$$RCOONa + HOH \rightarrow RCOOH + NaOH$$

and the free fatty acid as well as the alkali hydroxide is formed, so that at equilibrium it is possible to have a number of ions in a soap solution, $R{-}COO^-$; OH^-; and H^+; Na^+; as well as $RCOOH$, H_2O, and $RCOONa$ molecules. However, it is obvious that the OH^- ions will be present in greater amounts than the H^+ ions,

since a considerable number of the latter have been used up in forming non-ionized fatty acid molecules. The solution as a whole, then, will possess more or less pronounced alkaline properties. At one time detergent power of soap solutions was erroneously believed by some investigators to be due entirely to the alkali set free by the hydrolysis. The extent and importance of this hydrolysis is now considered to be less than the early work indicated.

The work of McBain and associates [24] has demonstrated that soap solutions represented a system in which ordinary electrolytes, colloidal electrolytes and neutral colloids were in general all present and that all three classes of solute played a part in determining the final properties of the soap solution. Probably both neutral and ionized colloidal micelles, formed from the combination of a fatty acid anion combined with a fairly large number of molecules of neutral soap, are active in contributing to the detergent and emulsifying properties of soap solutions. The low surface tension of soap solutions is also of great importance in the performance of soaps as insecticides and as spray adjuvants. The most efficient soaps are those formed from the fatty acids having between six and eighteen carbon atoms. Calcium and magnesium soaps are insoluble in water, and make up the precipitate observed when soaps are used in "hard" waters containing salts of these elements. Lead soaps which are also insoluble in water, may be formed in spray mixtures in which lead arsenate and soaps are present.

Soaps as Insecticides. Siegler and Popenoe [20, 21] advanced the hypothesis that the toxic action of soaps on insects was due to the action of the fatty acids produced on hydrolysis, rather than to the soap molecule itself. Previously it had been held that the combination of the soap with the small amount of free alkali present was responsible for the insecticidal action. The work of Siegler and Popenoe, however, which was confirmed by Tattersfield and Gimingham,[22] indicated that the toxic properties of the soaps made from various fatty acids paralleled the toxicity of the fatty acids themselves, and increased with increasing molecular weight up to a carbon chain of 10 or 12 carbon atoms, above which point the toxicity fell off. Dills and Menusan [23] made direct comparisons between the insecticidal properties of a series of saturated fatty acids and their corresponding potassium soaps and found that,

while the soaps in general were less toxic than the fatty acids alone, the toxicities of the acids and soaps were in the same general order, although the most toxic acid tested was capric (decylic), $C_9H_{19}COOH$, the C_{10} acid, while the most toxic soap was that of lauric (dodecylic) acid, $C_{11}H_{23}COOK$, the C_{12} acid, in the saturated acid series. [The soap of oleic acid (unsaturated) was more toxic than any of the soaps of the saturated acids.] The toxicity of the potassium soaps to plants decreased as the size of the molecule increased. Figure 16, from the paper by Dills and Menusan, shows the insecticidal properties of the various soaps.

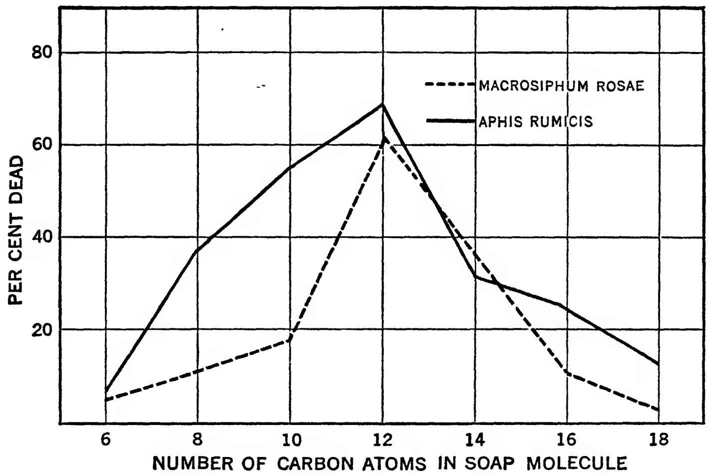

FIG. 16. Toxicity of 0.5 per cent potassium soaps to *Aphis rumicis* and *Macrosiphum rosae*. (From Dills and Menusan.)

These authors found little difference between the toxicity of the sodium and potassium soaps of oleic acid, although Fleming and Baker [25] found that against Japanese beetles sodium oleate was more toxic than the potassium salt. These authors found potassium myristate, $C_{13}H_{27}COOK$, the soap of a C_{14} acid, to be the most toxic. Attempts at correlating physical properties, such as surface tension, angle of contact, etc., to toxicity were not successful.

Many workers have tested the soaps of various natural fats against insects: as might be expected, the soaps of natural fats rich in toxic fatty acids show generally greater toxicity than those fats containing the less toxic fatty acids, although because of the

fact that many natural fats are mixtures of a number of fatty acid esters, clear-cut differences are often not apparent. Among the workers who have investigated this field are Fleming and Baker,[25] who found cottonseed oil, which contains esters of palmitic, oleic, and linoleic acids, to be superior to soybean, linseed (containing esters of linolenic and linoleic acids), castor (mainly ricinoleic acid esters), peanut, and coconut oil. Dills and Menusan [23] found olive oil soap (high in oleic acid) to be most toxic with little difference between the soaps prepared from coconut, menhaden, and cottonseed oils, although castor oil soap was decidedly less toxic to the insects used.

Van der Meulen [26] found that while neither surface tension nor viscosity of fresh soap solutions was correlated with toxicity to insects, the type of film formed on the surface of a soap solution after standing exposed to the air was a rough index of the toxicity of the solution; that is, the tougher and more tenacious the film formed, the greater the toxicity. This would indicate that orientation and denaturation had taken place in the soap solution. Fulton's work [27] indicated that the more rapid the rate of evaporation from the surface of a soap solution the less the toxicity of the solution. Tattersfield and Gimingham [22] found the partition coefficient (between two immiscible solvents) to be a measure of the toxicity of certain fatty acids. To date, however, there appears to be no physical or chemical test or measurement by which the insecticidal value of a soap may be measured with any degree of accuracy.

The various oils and fats from which insecticide soaps have been made may be listed briefly:

ANIMAL FATS	VEGETABLE OILS
Whale	Linseed
Fish	Hempseed
Cod	Cottonseed
Herring	Rapeseed (Colza)
Menhaden	Castor bean
Sardine	Coconut
Degras (wool grease)	Soybean
Lard	Palm
Neatsfoot	Corn

Reactions of Soaps with Other Insecticides. In all equilibrium reactions, the removal of one of the products causes the reaction to proceed to completion; hence the solvents for the fatty acids, such as the hydrocarbon oils, cause the hydrolysis of soap to approach completion. Thus in mineral oil emulsions, soaps as such are probably not present in any considerable quantity, a fact which is of considerable importance in the use of soaps in such emulsions.

In combination with inorganic insecticides, such as lead or calcium arsenate, a double decomposition takes place, resulting in the formation of insoluble lead and calcium soaps and soluble aresenic. Combinations of this nature should be avoided for obvious reasons. Roark [28] has shown that, since the pyrethrins (the active principles of pyrethrum) are themselves esters, the action of alkaline solutions, such as soap solutions, is to break down the esters with the subsequent formation of alkaline salts of the organic acid portion of the pyrethrin molecule. Hence soap and pyrethrum preparations should not be combined, particularly if the mixture is to be stored for any length of time. Various other materials have, at one time or another, been proposed as combination sprays with soap. In most of these the soap is present as an agent to assist in the wetting and spreading of the liquid, and will be discussed later.

COAL TAR DERIVATIVES

The use of coal tars (sometimes called carbolineums, tar creosotes, tar distillates, tar oils) as insecticides is of comparatively recent origin. According to Hurt,[29] coal tar preparations for this purpose had their origin either in Germany or Holland shortly before 1920, and were introduced into England about this time. As dormant sprays these preparations were so successful that their use spread rapidly, and at present they are widely used as sprays in many areas, particularly in Europe, where the cost of such products is less than petroleum.

Classification of Coal Tars. Coal tar is the term used to describe the distillate obtained from the destructive distillation of coal and is a by-product in the production of coke and illuminating gas. Probably no product used as an insecticide is more variable in composition, for the composition depends not only on the type

and composition of the coal used for coking, but on the temperature and method of distillation. Usually the crude tar obtained from the coking process is subjected to fractional distillation, during which process it is separated into several fractions. These fractions or "cuts" are not standardized, so that preparations of different manufacturers bearing the same designation may have been distilled at quite different temperatures, and hence have entirely different properties.

The fractions usually separated, with their approximate boiling ranges and general composition, are given below:

Up to 210° C.—Light oil—benzines, toluene, xylene
210°–240° C.—Middle or carbolic oil—phenols—naphthalene
240°–270° C.—Heavy or creosote oil
Above 270° C.—Anthracene oil—anthracene

These figures should not be considered as exact, for individual distillers usually divide the fractions according to specifications of the consumer.

Chemistry of Coal Tars. The chemistry of coal tars is extremely involved, and little is known as to the exact composition of much of the distillate. It is helpful to bear in mind in considering the chemistry of coal tars that many series of compounds are present, each compound in a given series being similar to the other members, but differing slightly in melting and boiling point from the others; thus it is impossible sharply to differentiate between fractions separated by ordinary distillation. The groups of hydrocarbon compounds present in petroleum oils are also present in the tar oils, the chief differences chemically between the two being in the different proportions of the different groups present. In the low-boiling tar oils, the paraffins and naphthenes are present in small quantities, but are not present in appreciable amounts in the higher-boiling tar oils (we are speaking now of the tars produced by the ordinary high-temperature carbonization of coal; low temperature coal carbonization produces a tar of quite different characteristics). The predominant hydrocarbons in tar oils belong to the aromatic series.

In addition to the hydrocarbons, tar distillates contain certain series of hydrocarbon derivatives having acidic or basic properties.

One of these groups is the tar acids, hydroxyl aromatic derivatives (phenols and cresols). The tar bases are mainly aromatic nitrogenous derivatives, such as quinoline.[30] The tar acids and bases may be extracted from the other materials present by treatment with acid and alkali solutions. Certain substances present in tar distillates are crystalline at relatively low temperature; these are usually separated by chilling.

Hartzell, Harman, and Reed [31] as well as Martin [30] and Ginsburg and Driggers [32] have discussed coal tar distillates as insecticides at considerable length. Fieldner et al.[33] and Worthley and Steiner [34] have discussed the differences between high- and low-temperature tar distillates. The most important differences between these two types of distillates are in the distribution of the constituents; low temperature tars containing more acids, paraffins, and naphthenes than the high-temperature tars, while the latter contain more aromatics, bases, and olefines. Low-temperature distillates are not produced in such large quantities as the high-temperature products, and the work of Worthley and Steiner apparently represents the first use of this material as an insecticide.

Little work has been done on the chemical constituents of coal tar which are responsible for its insecticidal action. Tutin [35] found that the most ovicidal fraction tested was the liquid, neutral material boiling from 280° to 360° C. This material was also less phytocidal than the other fractions tested. The presence of tar acids was a disadvantage from an egg-killing point of view. The source of the tar was found to have no bearing on its ovicidal properties.

Weiss and Downs [36] give in Table 4 the composition of representative coke-oven tars.

Of the compounds listed in the table as being present in coal tar distillates, Siegler, Munger, and Smith [37] have found the following to be relatively non-toxic to codling moth larvae when used as stomach poisons: acenaphthene, anthracene, dimethylnaphthalene, fluorene, and phenathrene.

Standardization of Coal Tar Distillates as Insecticides. In spite of the fact that relatively little is known concerning the toxic properties of tar distillate fractions, certain workers have set up tentative standards for such preparations to be used as insecticides. Such is the variation in manufacturing procedure that prospective

purchasers should investigate at least the boiling range of any product offered for use.

TABLE 4

COMPOSITION OF REPRESENTATIVE COKE-OVEN TARS
(From Weiss and Downs)

	Per cent by weight of dry tar
Light oil	
Crude benzene and toluene	0.3
Coumarone, indene, etc.	0.6
Xylenes, cumenes, and isomers	1.1
Middle and heavy oils	
Naphthalene	10.9
Unidentified oils in range of naphthalene and methylnaphthalenes	1.7
α-monomethylnaphthalene	1.0
β-monomethylnaphthalene	1.5
Dimethylnaphthalenes	3.4
Acenaphthene	1.4
Unidentified oil in the range of acenaphthene	1.0
Fluorene	1.6
Unidentified oil in range of fluorene	1.2
Anthracene oil	
Phenanthrene	4.0
Anthracene	1.1
Carbazol and kindred nonbasic nitrogen-containing bodies	2.3
Unidentified oils, anthracene range	5.4
Phenol	0.7
Phenol homologs (largely cresols and xylenols)	1.5
Tar bases (mostly pyridine, picolines, lutidines, quinolines and acridine)	2.3
Yellow solids of pitch oils	0.6
Pitch greases	6.4
Resinous bodies	5.3
Pitch (238° C. melting point)	44.7
	100.0

Hartzell, Harman, and Reed [31] have set up the following specifications for a satisfactory tar distillate for dormant sprays on fruit trees.

1. "It shall be derived from tar secured from bituminous coal, the latter having been heated to high temperature in gas retorts or by-product coke ovens in the making of illuminating gas.

2. "Based on freedom from water the tar oil shall distil within the following limits:

At temperatures up to	410° F. (210° C.)	not more than	1 per cent		
" " " "	455° F. (235° C.)	" " "	10	"	"
" " " "	671° F. (355° C.)	" " "	65	"	"

3. "It shall not contain more than 3 per cent water.

4. "It shall not contain more than 10 per cent tar acids and less than 5 per cent is to be preferred.

5. "It shall remain free from crystals on standing 3 hours at 41° F. (5° C.) with occasional stirring.

6. "Tests 2, 3, and 4 shall be made in accordance with the standard methods of the Society of Testing Materials."

Martin [30] suggests that tar distillates be grouped into two classes according to the type of insect against which they are to be used, and discusses at some length the desirable qualities, and methods of testing (see Chapter XIV).

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CHAPTER IX

FUMIGANTS

Fumigants include those chemical substances which exert their insecticidal action in the gaseous state. Such materials may be in form of solid, liquid or gas when applied, but in whatever state they are used they must possess the property of ready volatility. A wide variety of chemicals has been used as fumigants; those that will be considered here have in common a high volatility, combined with effective insecticidal action. Fumigation is commonly used as a means of disinfecting large closed spaces, such as dwellings and ships. Although certain of the materials used as insecticides have value as germicides, not all are useful in this connection. In the present discussion only those fumigants acting as insecticides will be considered.

Hydrocyanic Acid (hydrogen cyanide; prussic acid)—HCN. This material in the pure state is a colorless gas at temperatures above 26° C. (78.8° F.), the boiling point of the liquid, which is also colorless. It has an odor said to be similar to that of bitter almonds. The specific gravity of the gaseous form is very nearly the same (0.9348) as that of air at ordinary room temperatures, and it has a vapor pressure of 738.8 mm. at 25° C. As a fumigant, hydrogen cyanide is either applied directly in the liquid or gaseous state, or the gas is generated by chemical means from one of several salts. In small scale operations, such as the fumigation of dwellings and greenhouses, the gas is usually generated on the spot from one of its salts; this method is convenient, quick, and cheap. For larger spaces, such as mills and warehouses, in which fumigation is carried out at regular intervals, the compressed gas is often used, and may be piped to various parts of the building to facilitate application.

Liquid hydrogen cyanide is marketed in several forms: in cylinders as the pure liquid; absorbed on discs of porous cardboard, which are scattered about in buildings and slowly give up their absorbed gas; and absorbed on other materials, such as diatomaceous earth. The chief advantages of such preparations as the

latter are the convenience with which they may be distributed, and the relatively slow rate at which the gas is liberated. The use of such materials requires the aid of extremely efficient gas masks, of course.

Due to the extremely poisonous nature of hydrogen cyanide, great caution should always be exercised in its use, and under no circumstances should it ever be used by inexperienced persons.

Chemistry of Hydrogen Cyanide. Hydrogen cyanide may be produced from a number of its salts by the action of acid, according to the reaction

$$KCN + 2H_2SO_4 \rightarrow KHSO_4 + HCN$$

The sodium salt is at present more widely used than potassium cyanide, because of its lower price, and because the proportion of CN is greater (39.9 per cent in KCN; 53 per cent in NaCN). With concentrated acid, carbon monoxide is formed in large quantities [1] according to the reactions

$$HCN + 2H_2O \rightarrow HCOOH + NH_3$$
$$HCOOH \rightarrow H_2O + CO$$

In practice, in order to secure the maximum amount of hydrogen cyanide, diluted acid is used, in the following proportions:

Commercial (66° Bé.) H_2SO_4	1½ pints
Water	3 pints
Sodium cyanide	1 pound

The acid should be poured carefully into the required amount of water and the two thoroughly mixed in a container not attacked by acid, such as an earthenware crock. When all is in readiness, the operator drops the sodium cyanide into the acid solution. The usual procedure in fumigating a building is to prepare the containers of acid in advance and, starting at the part of the building farthest from the exit, work rapidly toward the door, dropping the cyanide in each container in succession. The operator should be provided with an efficient gas mask, and all possible precautions should be taken to prevent leaks of the gas into adjoining buildings. Several schemes have been used to delay the reaction between the acid and the cyanide salt, to allow greater time for the operator to leave the building. These include the use of paper bags into which

the required amounts of sodium cyanide are weighed. When such bags are dropped into the acid solution, several minutes elapse before the solution penetrates into the interior of the bag. Weighed amounts of sodium cyanide are also sold sealed in zinc foil; when added to the acid, the time required for the acid to penetrate the metal is sufficient to allow the operator to get to safety. The most usual form of sodium cyanide used in this country is in the form of "eggs" of the compressed salt, each "egg" weighing one ounce.

Hydrogen cyanide may also be generated by the action of moisture on calcium cyanide.

$$Ca(CN)_2 + 2H_2O \rightarrow 2HCN + Ca(OH)_2$$

According to Metzger,[2] this material, which is made from calcium carbide and liquid hydrocyanic acid, is probably not calcium cyanide, $Ca(CN)_2$, but the acid cyanide, $CaH_2(CN)_4$, the reaction being

$$CaC_2 + 4HCN \rightarrow CaH_2(CN)_4 + C_2H_2$$

The decomposition of this material would then take place as follows:

$$CaH_2(CN)_4 + 2H_2O \rightarrow 4HCN + Ca(OH)_2$$

The product, whether it be calcium cyanide or calcium acid cyanide, is rapidly decomposed when exposed to moist air. Metzger [2] states that when the powdered material is spread in extremely thin layers about three-quarters of the hydrocyanic acid content has been evolved in one-half minute, and practically all of it in one minute. This evolution of gas takes place on exposure to air even if the humidity is 25 per cent or less.

For certain uses, such as greenhouse fumigation, this material is extremely convenient. It is scattered on the walks between the beds in the greenhouse in the evening and allowed to react during the night. It is said that by morning, the gas will have practically disappeared from the house. The commercial preparations of calcium cyanide yield about 55 per cent by weight of HCN, and obviously should be kept in moisture-tight containers.

Because of the highly toxic nature of gaseous HCN "warning" gases are sometimes added to warn individuals of the presence of the hydrogen cyanide. Warning gases may be classified as follows:

1. Odoriferous substances.
2. Irritants.
   a. Eye irritants or lachrymators
   b. Nose and throat irritants
   c. Sternutators

An ideal warning gas would be one which would warn under any and all conditions. In particular, the warning gas should behave as nearly as possible like the toxic gas; that is, it should diffuse at the same rate and have the same specific gravity. Unfortunately, no such perfect warning gas has yet been found. Chloropicrin and cyanogen chloride are two substances which have been most widely used as warning gases, particularly the former, which is a lachrymator (tear gas). Even chloropicrin, however, does not diffuse at the same rate as hydrogen cyanide, and is absorbed by certain materials to a considerably greater extent than the fumigant itself. Cases have been recorded in which the intense irritation caused by the tear gas has caused temporary blindness, preventing the worker from finding his way out of a fumigated building. Fatalities have occurred in this manner.

The treatment of citrus trees is a rather specialized field of fumigation. In carrying out this process, the tree to be fumigated is first covered with a cloth tent and hydrocyanic acid gas introduced in the proper amount. Quayle[3, 4] has described various methods for carrying out such fumigations, including the use of calcium cyanide.

Cupples, Young, and Busbey have prepared bibliographies of cyanide compounds used as insecticides,[5] which include over a thousand literature citations on the subject of cyanide compounds used as insecticides.

Chloropicrin (nitrochloroform, trichloronitromethane)—CCl_3NO_2. This material, known during the first World War as vomiting gas, acquinite, G-25, S-1, and PS is a colorless liquid with a boiling point of 112.4° C., melting point −64° C., specific gravity 1.692 0°/4° C.,[6] and a vapor pressure of 23.9 mm. at 25° C. It was first prepared by Stenhouse[7] in 1848 by adding an aqueous solution of picric acid to an excess of bleaching powder. Apparently, little further investigation of the compound was made until the first World War, when it was used on a large scale in shells, both as a

lachrymatory and a lethal gas, generally mixed with other gases. The liquid volatilizes slowly and at relatively low concentrations causes intense irritation to the eyes, and in addition possesses the peculiar property of inducing vomiting, a fact which made it particularly useful in warfare, since it caused the soldiers to remove their masks and thus succumb to the other, more toxic gases with which it was usually mixed.

The first use of chloropicrin as an insecticide was proposed in 1907 in Austria. Moore [8] first tested chloropicrin as an insecticidal fumigant in 1917, and it has since found considerable application, particularly in mills and warehouses. It has recently been used as a soil fumigant and disinfectant, for, unlike hydrocyanic acid, chloropicrin possesses some fungicidal and bactericidal properties. It is superior to certain other fumigants in its complete freedom from fire and explosion hazards, ability to penetrate bulk commodities, non-reactivity with metals, fabrics and colors under fumigating conditions, and has a pronounced odor and lachrymatory effect, so that no "warning" gas need be added. It is slower in action than hydrocyanic acid, is relatively toxic to living plants and seeds, and its odor persists and is removed with some difficulty.[6]

The use of chloropicrin as a warning gas in conjunction with hydrocyanic acid has already been mentioned. For this purpose only a small percentage of chloropicrin is necessary. When used alone, the dosage of chloropicrin employed depends on several factors, and no general statement may be made. Chloropicrin has also been used in the form of water emulsions with soap as sprays to control soil insects, and is sometimes applied directly into holes made in greenhouse beds for the control of nematodes. Due to its high toxicity to living plants, it cannot be used for this purpose when plants are growing in the same house.

Cotton [9] and Cotton and Young [10] have found that mixtures of chloropicrin and carbon dioxide were considerably more effective than the same concentrations of chloropicrin alone.

Roark [6] and Roark and Busbey [11] have prepared extensive bibliographies of chloropicrin as an insecticide.

Carbon Disulfide (carbon bisulfide)—CS_2. Carbon disulfide is a colorless liquid, melting point $-108.6°$ C., boiling point 46.3° C., with a specific gravity of 1.263 20°/4° C., and a vapor

pressure of 357.1 mm. at 25° C. It is readily volatilized at ordinary room temperatures, and the vapor is 2.63 times as heavy as air.[12] The vapor, which has an unpleasant odor, is extremely inflammable, and is explosive when mixed with air over a wide range of concentrations. Further, the vapor explodes spontaneously when heated by coming in contact with steam pipes or other hot surfaces, so that the use of carbon disulfide must always be attended with great caution.

Carbon disulfide is manufactured by the direct reaction of sulfur vapor and coke in an electric furnace according to the reaction

$$C + 2S \rightarrow CS_2$$

As an insecticide, carbon disulfide was apparently first used in 1854 by Garreau in France,[13] although for many years Doyère was credited with the discovery.[12] Highly toxic to all forms of life, carbon disulfide is an effective insecticidal fumigant, and has been rather widely used in houses and warehouses. Carbon disulfide is toxic to plants and certain seeds,[12] and therefore it is not recommended for greenhouse fumigation. Shepard, Lindgren, and Thomas [14] found carbon disulfide less toxic to *T. confusum* than chloropicrin, but more toxic than carbon tetrachloride and ethylene dichloride.

Carbon disulfide is also frequently used as a soil insecticide, either as an emulsion with soap, alcohol and oil, or by placement into holes in the soil.[15] O'Kane [16] has made a detailed study of the diffusion of carbon disulfide in soil.

Carbon Tetrachloride (tetrachloromethane)—CCl_4. This material is a colorless liquid boiling at 77° C., made commercially by the reaction between sulfur monochloride and carbon disulfide in the presence of iron as a catalyst.

$$CS_2 + 2S_2Cl_2 \rightarrow CCl_4 + 6S$$

Unlike carbon disulfide, carbon tetrachloride is not inflammable, and is often used in fire extinguishers to smother flames. This property makes carbon tetrachloride an extremely safe insecticidal fumigant, but unfortunately its toxicity to insects is relatively low. Morse [17] compared the tetrachloride with the disulfide and found the former easier to use, although it has been

shown that to secure a 99 per cent kill of *T. confusum* at 20° C. more than five times as much of the tetrachloride was necessary.[14] The specific gravity of the gas is 1.6486, and the vapor pressure is 114.5 mm., both at 25° C.

At present the use of carbon tetrachloride as a fumigant is limited to operations where a fire hazard is present, or in small-scale home fumigation where the increased cost is not a serious drawback.

Back and Cotton [18] and Roark [19] have suggested the use of combinations of carbon tetrachloride and ethyl acetate and with ethylene dichloride, and the latter mixture has been widely adopted.

Ethylene Dichloride (1, 2, dichloroethane)—$C_2H_4Cl_2$. This material, although synthesized from ethylene, does not contain an ethylene linkage (double bond) and, therefore, should be designated by the more correct name, 1, 2, dichloroethane, the formula being $CH_2Cl—CH_2Cl$. This should not be confused with dichloroethylene (1, 2, dichloroethene), $ClHC = CHCl$, boiling point (cis form) 48° C. (trans form) 60° C. It is a colorless liquid, boiling at 83.5° C., melting point −36° C., density 1.2569 20°/4° C., vapor pressure 79.6 mm. at 25° C., is non-corrosive to metals and at ordinary temperatures is not dangerously inflammable. It possesses an odor similar to that of chloroform.

Ethylene dichloride was first synthesized by four Dutch chemists, Deimann, Van Troostwyk, Bondt, and Louwrenburgh, in 1795. For many years the compound was known as "oil of the Dutch chemists." It is a good solvent for oils, waxes, certain alkaloids, and is chiefly used for this purpose.[20] Commercially, dichlorethane is produced as a by-product of the production of ethylene chlorhydrin from ethylene and chlorine water.

Ethylene dichloride was suggested as an insecticidal fumigant in 1927 by Cotton and Roark [19] with carbon tetrachloride in the proportion 3 : 1, and the combination has been reported as being highly effective. A chemical study of such mixtures has been reported by Young and Nelson.[21] The boiling points of the two substances are approximately the same, so that they are volatilized at nearly equal rates from such mixtures. Mixtures of these two compounds, as well as mixtures of ethylene dichloride and trichloroethylene, are relatively safe fumigants, even in the hands of

inexperienced persons, because of their freedom from fire hazard and their relatively low toxicity to human beings.

Recently, ethylene dichloride has been tested as a means of controlling the peach tree borer as a substitute for paradichlorobenzene.[22] For this purpose an emulsion of ethylene dichloride with potash fish oil soap is used. This application has not been tested thoroughly as yet, but it appears to offer certain advantages over the older procedure.

The literature concerning ethylene dichloride has been collected by Gersdorff.[20]

Trichloroethylene (trichloroethene)—C_2HCl_3. This compound, prepared from acetylene tetrachloride by treatment with bases, has the formula $ClHC = CCl_2$. It is a colorless liquid with a boiling point of 87° C., a density of 1.4556 25°/4° C., and a vapor pressure at 25° C. of 73 mm. The pure material decomposes rather readily when exposed to light, yielding phosgene (carbonyl chloride) and hydrochloric acid.

Trichlorethylene, like carbon tetrachloride, is not inflammable, and it has been suggested by Back and Cotton [23] as an insecticidal fumigant with ethylene dichloride in the proportion of three parts of the dichloride to one of trichloroethylene. In general behavior as a fumigant, trichloroethylene apparently is quite similar to carbon tetrachloride, although it is considered to be slightly more toxic.

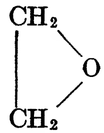
Tetrachloroethane—$C_2H_2Cl_4$. The compound, $Cl_2HC—CHCl_2$, exists in two forms, the symmetrical (1, 1, 2, 2, tetrachloroethane), with a boiling point of 146° C. and a density of 1.600 20°/4° C., and the unsymmetrical (1, 1, 1, 2, tetrachloroethane) with a boiling point of 130° C. and a density of 1.588 20°/4° C. Apparently the former compound is the one usually referred to in the literature as a fumigant. This is obtained by passing acetylene and chlorine into antimony pentachloride.

First used as a fumigant against the white fly in 1915, it has been further investigated by Lloyd.[24] It has been used with some success as a greenhouse fumigant, although it is toxic to certain plants.

Propylene Dichloride (1, 2, dichloropropane)—$C_3H_6Cl_2$. Propylene dichloride, $CH_2ClCHClCH_2$, boiling point 96.8° C., density 1.159 20°/20° C., is made by adding chlorine to propylene. It has

been suggested as an insecticidal fumigant by Hutson,[25] and apparently behaves in a manner similar to ethylene dichloride, although it has a considerably higher boiling point.

Ethylene Oxide (1, 2, epoxyethane)—$(CH_2)_2O$. This compound, a gas at ordinary room temperature, has a boiling point of 10.7° C. and a density of 0.887 7°/4° C. The structural formula is



and it may be made by heating a solution of ethylene chlorhydrin with a base and distilling the oxide as formed. The compound is very reactive at high temperatures, and is inflammable.

Cotton and Roark [26] first proposed the use of ethylene oxide as an insecticidal fumigant in 1928, and reported that it was not highly toxic to man, and had the advantage over certain other fumigants because its low boiling point permitted use at relatively low temperatures. These authors found that ethylene oxide vapors are toxic to seeds, seriously affecting germination.

Further investigation led to the use of mixtures of 90 per cent carbon dioxide and 10 per cent ethylene oxide (U. S. patent 2,024,027). The addition of carbon dioxide reduced the inflammability of the ethylene oxide so that there is no fire hazard, and such mixtures are now rather widely used as fumigants in warehouses, mills, etc.

Young and Busbey [27] have compiled a bibliography of ethylene oxide as a fumigant.

Propylene and Cyclohexene Oxides. A colorless liquid boiling at 35° C., with a density of 0.831 20°/20° C., propylene oxide (CH_3CHOCH_2) has somewhat similar properties to ethylene oxide and has been suggested as an insecticidal fumigant, but up to the present time has not been used to any extent. Cyclohexene oxide has been patented (U. S. 2,101,587) as a fumigant for stored products, but apparently has not been tested on a large scale.

Methyl Bromide (bromomethane)—CH_3Br. Methyl bromide, which may be made from sodium bromide, methyl alcohol and sulfuric acid, is a gas at ordinary temperatures, the boiling point of the liquid being 4.6° C. The vapor pressure of the gas at 25° C. is

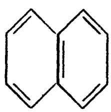
760 mm. It is not inflammable at the concentrations usually used (below 13.5 per cent according to Jones [28]). The low boiling point of the liquid form makes methyl bromide, like ethylene oxide, particularly adaptable to fumigations at low temperatures.

Methyl bromide was apparently first used as an insecticidal fumigant in France in 1932. Lepigre [29] gives a review of the early work in this connection. In this country, Fisk and Shepard [30] and Shepard and Buzicky [31] have made extensive studies of the action of methyl bromide as a fumigant. These authors conclude that methyl bromide penetrates extremely well into stored products, and is not highly toxic to living plant tissue, a fact confirmed by Donohoe and Johnson.[32] Phillips et al [33] have investigated the effect of methyl bromide on apples.

Apparently methyl bromide, although one of the newest of the fumigants, has considerable potential use.

Dichloroethyl Ether—$C_4H_8Cl_2O$. Two forms of dichloroethyl ether exist, β, β' dichlorodiethyl ether (1-chloro-2-(β chloroethoxy) ethane), with a boiling point of 178° C., and α, β-dichloroethyl ether (1, 2, dichloro-1-ethoxyethane), boiling point 143° C. Of these, the former has been used as an insecticidal fumigant, particularly in soil, where the high boiling point allows the fumigation process to proceed over a considerable length of time. Roark and Cotton [34] found dichloroethyl ether to be among the six best fumigants from the standpoint of toxicity among a large number of organic compounds tested. Wilcoxon and Hartzell [35] have reported that this material could be used successfully as a greenhouse fumigant, although certain plants, such as roses, carnations and peaches, were easily injured by it.

Naphthalene—$C_{10}H_8$. This compound, having the structure



is the largest single constituent of coal tar. A white, glistening crystalline solid, melting point 80° C., boiling point 218° C., and a vapor pressure of 0.10 mm. at 25° C., naphthalene is secured from certain fractions of coal tar distillates by cooling and centrifugation ("whizzing," hence "whizzed" naphthalene). The purer grades are subjected to sublimation. For a solid, naphthalene possesses

a relatively high volatility and, if placed in a closed container or room, readily saturates the air surrounding it. It is not soluble in water, but is easily soluble in a variety of organic solvents such as alcohol, benzene and ether.

To most people, naphthalene is probably the most familiar of all insecticides, for as "moth balls" it has been a household necessity for generations. In 1936, 16,500,000 pounds of naphthalene were consumed in the United States [36] principally against the clothes moth.

Recently, naphthalene has found increasing use as a greenhouse fumigant against thrips and the red spider. The naphthalene may be volatilized by heat, or by the method of Wilcoxon, Hartzell, and Youden,[37] in which the air of the greenhouse is recirculated through a solution of naphthalene of known concentration in a suitable solvent. This particular method of application has the advantage of accuracy of dosage.

Naphthalene is toxic to certain plants, as shown by the work of Hartzell.[38]

Paradichlorobenzene (1, 4, dichlorobenzene)—$C_6H_4Cl_2$. This compound is obtained as a by-product in the chlorination of benzene, and is sometimes called P. D. B. It is similar in appearance to naphthalene, and has a melting point of 56° C., and boils at 173° C. It has a vapor pressure of 1.0 mm. at 25° C. It is only slightly soluble in water, but freely soluble in ether, benzene, and chloroform. It is highly volatile and more is required to saturate a given volume of air than of naphthalene.

Apparently the first use of p-dichlorobenzene as an insecticide was by Blakeslee [39] in 1919 as a method for controlling the peach tree borer, *Sannonoidea exitosa* Say. For this purpose it is placed around the trunks of the trees, lightly covered with soil. More recently it has been applied as a suspension in certain vegetable oils.

p-Dichlorobenzene is also used as a household insecticide to protect woolens against the clothes moth in a manner similar to naphthalene. Roark [36] states that approximately 5,000,000 pounds of p-dichlorobenzene were used in this country in 1936.

Miscellaneous Fumigants. A wide variety of materials have been tried at one time or another as fumigants. Roark and Cotton,[34] for instance, report the testing of some 309 aliphatic compounds as fumigants; the most effective of these include in the

order of efficiency: ethyl mercaptan; isopropyl thiocyanate; ethyl isothiocyanate; allyl isothiocyanate; methyl disulfide; tertiary butyl bromide; epichlorhydrin; 2, chloroethyl ether; 2, bromethyl ethyl ether; allyl bromide; and 2, bromoethyl acetate. Of the 18 best fumigants, 15 contained chlorine, and 5 contained sulfur.

Other materials which have been used or recommended as fumigants include ethyl acetate, methyl and ethyl formates, monochloronaphthalene, potassium xanthate, and benzene. Inorganic materials, such as chlorine gas, sulfur dioxide, hydrogen sulfide, hydrogen phosphide, and nitrogen trichloride have also been suggested.

Nicotine, which has already been discussed, has been used rather widely as a fumigant for greenhouses. For this purpose, the nicotine is usually volatilized by heat.

Recently, Sullivan, Goodhue, and Fales [40] have developed a method for the production of *aerocolloids* or *aerosols* of a number of insecticides. By suitable means, such as spraying a solution of the insecticide upon a heated surface, the particles of active materials become very finely dispersed, and, due to their colloidal dimensions, remain in suspension in the air for considerable periods of time. Certain other materials, when burned to produce smoke or otherwise dispersed simultaneously with the insecticide, serve to lengthen the effective period of action. This aerosol method of fumigation appears to hold considerable promise, and further work will probably lead to a rather general application of this principle.

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Part III

Fungicides

CHAPTER X

FUNGICIDES

The control of fungi, because of the nature of the organisms involved, presents problems considerably different from those encountered in the control of insects. Since the fungi are plants themselves, the organism to be controlled is relatively similar in many of its properties, reactions, and responses to the host plant. For this reason materials applied to destroy fungi on plants are sometimes likely to injure the host plant.

The fungi are not mobile in the same sense as insects and for this reason their means of dissemination is different. The fungus spores, however, are widely distributed by various natural agencies, and are capable of being rapidly spread over a fairly wide area. To prevent the establishment of such spores, a fungicide may act to *protect* the plant; this in contrast to the *direct* toxic or *eradicant* action of fungicides upon the fungus organisms. Most sprays or dusts are applied to plants *before* the arrival of the fungus to the host plants and are thus *protective* in their action. Certain fungicidal preparations, such as seed and soil treatments and sprays for the peach leaf curl, for example, are applied to kill vegetative parts or spores of pathogens already present. These are examples of *eradicant* fungicides; it should be noted, however, that most seed treatments function in both ways.

Briefly, a good fungicide must be:

1. Lethal to pathogens at low concentrations.
2. Non-injurious to the host.
3. Easy to prepare and apply.
4. Inexpensive.
5. Adhesive, retaining its lethal action for a considerable period of time.
6. Non-poisonous to man.

Copper Compounds

Bordeaux Mixture. Although compounds of sulfur had been used as fungicides for many years, the introduction of the downy

mildew (*Peronospora viticola*) into French vineyards presented a serious problem, for none of the fungicides then in use was effective in controlling the disease. The mildew was first noticed in France in 1878, and within four years had established itself as a serious pest, threatening the entire French grape industry with destruction.

A number of workers naturally undertook to investigate this serious problem. It was found that a certain degree of control was obtained by treating the dormant vines and the supporting posts in the vineyard with iron or copper sulfate solutions. Millardet, one of those investigating the problem, noted in the autumn of 1882 that a few vines along the highways escaped injury. These were located near the city of Bordeaux, about Margaux, St. Julian, and Pauillac, in Medoc, in the Gironde. Investigating these vines, Millardet found that in this area it was the custom to sprinkle the first few rows of vines with a mixture of milk of lime and a salt of copper. This mixture was applied with brooms, and was placed on the leaves of the plants to give them the appearance of having been poisoned, to discourage children and travelers along the highways from stealing the grapes.

As lime alone had been used previously as a fungicide without success, it appeared to Millardet that the combination of lime and copper must be responsible for the protection of the vines from mildew. Following this observation, assisted by Gayon, professor of chemistry at Bordeaux, he carried out systematic investigations and finally, in 1885,[1] first described the preparation of Bordeaux mixture. The original mixture, to be applied with a broom, consisted of 8 kilograms of copper sulfate dissolved in 100 liters of water, to which were added 15 kilograms of quicklime suspended in 30 liters of water. Many formulas have since been suggested for Bordeaux mixture, and it has been accepted that the proportions of lime and copper sulfate may be varied according to the purpose for which the material is to be used. In this country, the formula usually calls for the use of hydrated lime; a 4–4–50 Bordeaux mixture, for example, consists of 4 pounds of copper sulfate and 4 pounds of hydrated lime made to 50 gallons of spray with water. Bordeaux mixture, when properly made, consists of a light blue gelatinous precipitate suspended in water. The precipitate is relatively stable, and remains in suspension for considerable time.

Chemistry of Bordeaux Mixture. Numerous workers have investigated the chemical reactions which take place between calcium hydroxide and copper sulfate in solution. It is obvious that a wide variation in the composition of the resulting mixture will result as the ratio between the components is changed. The early writers, in fact, recognized three types of Bordeaux mixture: "acid Bordeaux," which was supposed to contain a small amount of soluble copper and to have a faintly acid reaction; "neutral Bordeaux," in which the ratio copper sulfate to calcium oxide was approximately 1 : 0.3; and "alkaline Bordeaux," in which the ratio copper sulfate to calcium oxide was 1 : 0.5 or greater. This system of classification is no longer used.

Early workers assumed that the active principle of Bordeaux mixture was copper hydroxide $[Cu(OH)_2]$. This was disproved by Pickering [2] who was one of the first to make a thorough study of the reactions taking place in the preparation of Bordeaux mixture. He found that the composition of the precipitate was dependent on the amount of calcium hydroxide added per unit of copper sulfate, and concluded that a series of basic copper sulfates and basic copper-calcium sulfates was formed. He indicated that, when the ratio of copper sulfate to calcium oxide was 1 : 0.166, a double salt having the composition $[Cu(OH)_2]_3CuSO_4$ was formed; with a ratio of 1 : 0.181, $[Cu(OH)_2]_4CuSO_4$; 1 : 0.20, $[Cu(OH)_2]_9CuSO_4$; 1 : 0.269, $[Cu(OH)_2]_9Ca(OH)_2CuSO_4$; 1 : 1, $[Cu(OH)_2]_9CuSO_4[Ca(OH)_2]_3CaSO_4$. Butler [3] has summarized the earlier work on the chemistry of Bordeaux mixture.

More recent and more accurate work along similar lines has been done by Martin [4] who found that the initial product of the reaction between copper sulfate and calcium hydroxide at ordinary temperatures is a basic sulfate, $[Cu(OH)_2]_3CuSO_4$. This product is formed when less than 0.75 equivalent of calcium hydroxide has been added to one equivalent of copper sulfate. At this point, all of the copper sulfate has reacted with the calcium hydroxide, and further additions of the alkali cause decomposition of the $[Cu(OH)_2]_3CuSO_4$ salt, with the elimination of the sulfate ion, resulting in the formation of a blue hydrated cupric oxide (or hydroxide). This hydrated oxide retains a portion of the free sulfate present by adsorption. The course of this reaction is shown in figure 17.

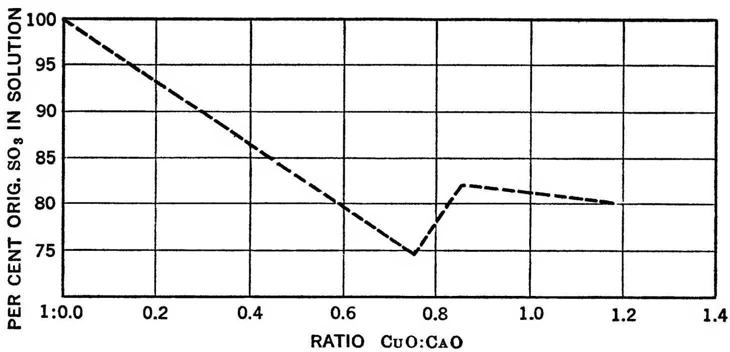

FIG. 17. Relation between sulfate radical remaining in solution and the CuO : CaO ratio in Bordeaux mixture. (From Martin.)

Martin also investigated the hydrogen-ion concentration of various mixtures of copper sulfate and calcium hydroxide, and found, as shown in figure 18, that there was a definite break in the

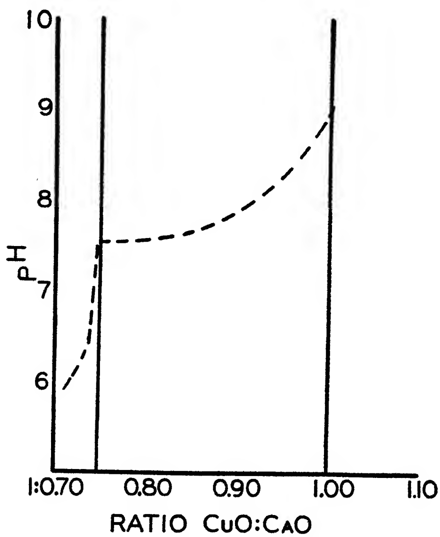

FIG. 18. Relation between the pH of Bordeaux mixture and the CuO : CaO ratio. (From Martin.)

titration curve when 0.75 equivalent of calcium hydroxide had been added to one equivalent of copper sulfate.

From this study Martin concluded that the formation of a basic sulfate having the formula $[Cu(OH)_2]_3CuSO_4$ took place

when 0.75 equivalent of calcium hydroxide was added, and that definite alkalinity, with complete decomposition of the basic sulfate, took place when the ratio of copper oxide to calcium oxide reached 1 : 1.

Martin further found that the cupric hydroxide formed from the basic sulfate ($[Cu(OH)_2]_3CuSO_4$), by the action of calcium hydroxide, was stabilized by the adsorbed sulfate ions, and, if washed repeatedly with carbon dioxide-free water, undergoes dehydration to form a brown cupric oxide.

Butler [3] has pointed out that, in mixtures containing from 0.125 per cent copper sulfate, the gelatinous precipitate becomes crystalline after standing for a short period. This crystallization occurs even when an excess of calcium hydroxide is present, and obviously affects the adhesiveness and rate of settling of the precipitate. The crystallization is retarded by the presence of such impurities as ferrous sulfate, calcium carbonate, and magnesium oxide or carbonate. The addition of certain other substances, such as sucrose, may also act to retard crystallization.

Several workers have investigated the physical methods of preparing Bordeaux mixture, among them being Butler [3] and Holland, Dunbar, and Gilligan.[5] Butler found that the physical state of the precipitate of Bordeaux mixture depended to a large extent on the dilution of the salts used and the manner in which they were brought together. Holland et al [5] found that the most readily suspended precipitate was formed when a dilute solution of copper sulfate was added to a concentrated suspension of lime. There has recently appeared on the market a finely ground form of copper sulfate, sometimes called "copper sulfate snow," which, by virtue of its state of division, goes into solution very readily and thus simplifies the process of making Bordeaux mixture. High grade chemically hydrated lime is now used almost exclusively, since it is possible to secure a uniform, finely divided product.

Reactions of Bordeaux Mixture. When Bordeaux mixture is applied to a plant surface and allowed to dry, the deposit does not undergo visible decomposition, as might be expected. Martin [4] found that there was a reaction between carbon dioxide of the air and the dried deposit of basic sulfate and hydroxide which prevented the formation of the less highly hydrated brown forms of copper oxide. The brown copper oxide was formed when a

Bordeaux mixture precipitate was first dried in an atmosphere free from carbon dioxide and then washed with carbon dioxide-free water. The exact nature of the products formed by the reaction has not been determined.

The excellent adhesive properties of Bordeaux mixture have usually been ascribed to the gelatinous nature of the precipitate. Martin, however, considers that the reaction between the precipitate and atmospheric carbon dioxide causes the formation of a highly resistant deposit.

Although deposits of Bordeaux mixture have been considered to be but very slightly soluble, Goldsworthy and Green [6] have found that the copper in the mixture dissolves in water at the rate of about 4 parts per million. This concentration has been shown to be too low to be harmful to most fungus spores, so that some other mechanism must be sought to explain how copper may exert its toxic action. Goldsworthy and Green found that, when deposits of Bordeaux mixture were exposed to rainfall, the toxicity of the deposits was gradually lessened, and that deposits stored in the laboratory for the same length of time did not lose their toxicity. They concluded that in "freshly deposited Bordeaux mixture residues there is present a component bearing available copper which is exhausted by washing with rains but not by aging. After it is lost, conidia that come to rest in contact with the residue are inhibited in germination but are not killed, and can germinate freely when removed from this contact. While it is still present, conidia take up copper before any visible evidence of vital activity is observed. From this it appears that the conidial cells are not capable of secreting a substance which will dissolve the inert copper of these washed residues."

Wilcoxon and McCallan,[7] in a more recent publication, indicate that sprayed films of Bordeaux mixture undergo a continual change in composition under the influence of rain and dew. "The excess lime of the mixture is carbonated quite rapidly,* and the subsequent leaching effect of rain removes calcium and sulfate at a greater rate than copper, leaving a residue richer in copper as the weathering proceeds. This change in composition is accompanied by the appearance of increased amounts of soluble copper. . . ." [(7, p. 157)]

* Carbonation was practically complete after two hours.

These authors found further that the carbonation of the excess lime could not explain the formation of soluble copper, since the latter did not appear until after the carbonation process was complete. It appears that the exact mechanism of the reaction is still in doubt, for Wilcoxon and McCallan do not agree with Reckendorfer's [8] conclusions that various carbonates of copper are formed by the atmospheric carbon dioxide. The question of the mechanism of the formation of soluble copper is particularly important, because the phytocidal action of copper sprays is apparently due to the element in soluble form.

Bordeaux mixture, because an excess of calcium hydroxide is usually present, cannot be combined with soaps, or with those organic insecticides (such as pyrethrum) which are decomposed by free alkali. Bordeaux mixture is a fairly efficient emulsifier and has been used in combination with various oils at times.

Dried Bordeaux Mixture and Related Materials. Since Bordeaux mixture, to be most effective, must be made up immediately before use, numerous attempts have been made to prepare it in the dried form, which would be considerably more convenient to use. Attempts to dry the precipitate as such have not been particularly successful, and, although dried Bordeaux mixture is on the market, the product is usually considerably inferior to that made immediately before use. Robinson [9] has suggested that the addition of casein in small amounts to the lime would make possible a more stable preparation. Hooker [10] has reported the preparation of colloidal copper hydroxide which in his hands was an efficient fungicide at relatively low concentration. Various copper-lime dusts have been recommended from time to time, using copper sulfate and calcium hydroxide in intimate mixtures. These have never been widely used, however. Recently, certain basic copper sulfates have appeared on the market. These will be discussed later.

Burgundy Mixture and Related Materials. Burgundy mixture, or soda Bordeaux, was first prepared by Masson [11] by allowing one part of copper sulfate pentahydrate to react with one or two parts of crystalline sodium carbonate in solution. The resulting product was similar in appearance to Bordeaux mixture and was first thought to contain copper carbonate. The work of Mond and Heberlein [12] and Pickering [13] has shown that, as in the case of

Bordeaux mixture, the composition of the precipitate depends upon the amounts and proportions of the reacting compounds. Pickering concluded that the reaction between the copper sulfate and sodium carbonate resulted in the formation of a basic carbonate, $[Cu(OH)_2]_3(CuCO_3)_2$, sodium sulfate, and carbon dioxide, which combined with the sodium carbonate to form the bicarbonate, $NaHCO_3$. Mond and Heberlein found that neutrality is reached when equi-molecular quantities of the two reactants are present, although part of the copper is in solution, even under these conditions, due to the presence of carbon dioxide. The reaction appears to be:

$$5CuSO_4 \cdot 5H_2O + 8Na_2CO_3 \cdot 10H_2O \rightarrow [Cu(OH)_2]_3(CuCO_3)_2 + 6NaHCO_3 + 5Na_2SO_4 + 99H_2O$$

According to Butler,[14] "acid" Burgundy mixtures are produced whenever less than 0.86 part of crystallized sodium carbonate is combined with one part of copper sulfate, and such mixtures contain both basic carbonate and basic sulfate. The basic carbonate is not stable, being converted into malachite, $Cu(OH)_2CuCO_3$. An excess of sodium carbonate retards the formation of malachite.

Sodium bicarbonate ($NaHCO_3$) has been used to react with copper sulfate in place of sodium carbonate. Mond and Heberlein [12] found that 0.625 gram of the bicarbonate was required to react with one gram of copper sulfate, and that the products formed were basic copper carbonate, basic copper sulfate, and carbon dioxide.

In actual practice, a large excess of sodium carbonate is as disadvantageous as an excess of soluble copper. Mixtures usually range from 10 : 10 : 100 to 10 : 14 : 100, although less concentrated mixtures have also been used. The first figure in these proportions refers to the weight in pounds of copper sulfate pentahydrate, the second to the weight in pounds of sodium carbonate ($Na_2CO_3 \cdot 10H_2O$), and the third to the final volume of water in gallons. Because of its phytocidal action, the use of Burgundy mixture is usually restricted to the more resistant plants, such as the potato. Butler [14] indicates that Burgundy mixture may be combined with either acid lead arsenate or calcium arsenate, although the latter is preferable. The chief advantage of

Burgundy mixture over Bordeaux mixture, freedom from gritty, insoluble residues, has been largely overcome by the use of high-grade hydrated lime in the latter.

Eau Celeste: Cuprammonium Compounds. The discovery of Bordeaux mixture stimulated a search for similar preparations in the hope of finding a copper-containing mixture of superior qualities. This work resulted, as we have seen, in the introduction of Burgundy mixture, in which the alkali of Bordeaux mixture, calcium hydroxide, was replaced by sodium carbonate. In 1886 Audoynaud [15] prepared a similar modification, using ammonium hydroxide and copper sulfate. The resulting mixture had a beautiful blue color, and was named "Eau Celeste," presumably because of its sky blue tint.

When ammonium hydroxide is added to a solution of copper sulfate, a light blue, gelatinous precipitate is formed which, according to Butler,[16] is basic copper sulfate, according to the reaction:

$$3CuSO_4 \cdot 5H_2O + 4NH_4OH \rightarrow [Cu(OH)_2]_2CuSO_4 + 2(NH_4)_2SO_4 + 15H_2O$$

As the addition of ammonium hydroxide continues, however, the precipitate first formed is dissolved, forming a very deep blue solution. Butler [16] considers that a cuprammonium complex is formed at this stage:

$$[Cu(OH)_2]_2CuSO_4 + 2(NH_4)_2SO_4 + 8NH_4OH \text{ (in excess)} \rightarrow 3Cu(NH_3)_4SO_4 \cdot H_2O + 9H_2O$$

Bedford and Pickering,[17] nevertheless, consider the correct formula for this compound to be $Cu(NH_3)_3SO_4 \cdot 2H_2O$.

The cuprammonium salt is apparently readily decomposed,

$$3Cu(NH_3)_4SO_4 \cdot H_2O + H_2O \rightarrow [Cu(OH)_2]_2CuSO_4 + 2(NH_4)_2SO_4 + 8NH_3$$

with the release of ammonia, to form the basic sulfate. It follows, then, that when *eau celeste* is applied as a spray, the deposit consists mainly of basic copper sulfate, plus some ammonium sulfate.

Various other cuprammonium mixtures have been advocated. Butler has divided these into two groups: those in which the com-

pounds formed are mainly cuprammonium hydrates, formed when metallic copper is allowed to react with an excess of ammonium hydroxide, or when Burgundy mixture sometimes called "Modified *eau celeste*" or copper carbonate (malachite) is so treated. The second group includes those mixtures in which the main constituent is cuprammonium carbonate. These are formed when ammonium carbonate reacts with copper sulfate (Johnson's mixture), malachite, cuprammonium sulfate ($Cu(NH_3)_4SO_4 \cdot H_2O$ mentioned above), or the basic carbonate of Burgundy mixture. The cuprammonium hydrate and carbonate are considerably more stable than the cuprammonium sulfate, and after drying yield copper hydrate and copper carbonate, respectively.[16]

None of the cuprammonium mixtures have found wide application; they are considerably more likely to produce plant injury than Bordeaux mixture, for which they are useful substitutes only in cases of extremely heavy fungus infestations on resistant plants.

Copper Compounds Related to Bordeaux Mixture. Within the past few years, a variety of new "basic" copper products have appeared on the market. These have been sold under a variety of names, and it is difficult to determine their chemical nature. It would appear that a copper basic or oxychloride, $[Cu(OH)_2]_3CuCl_2 \cdot 4H_2O$, and the basic chlorides having the formula $[Cu(OH)_2]_xCuCl_2$, where x may be 3 or 4, are important constituents of certain commercial fungicides. These are related to the basic sulfates which have been mentioned previously. The basic sulfate and mixed basic sulfate-chloride are also supposed to be the active compounds in certain proprietary copper materials. At present, little is known of the chemistry of such derivatives, and although trials of their effectiveness are under way at the present time it is probably too early to evaluate them. It should be noted, however, that the manufacturers are attempting to produce dried preparations which will be closely related, in both constitution and performance, to Bordeaux mixture, Burgundy mixture, and the cuprammonium mixtures.

Copper Phosphate—$Cu_3(PO_4)_2$. Young and Beckenbach [18] and Roberts et al.[19] have suggested the use of copper phosphate as a fungicide. This compound may be prepared by dissolving the basic copper carbonate in dilute phosphoric acid and heating to

70° C., and occurs as blue rhombic crystals. It is relatively insoluble in water, and it was soon discovered to have poor powers of adherence to plant surfaces. Roberts et al.[19] indicated that the addition of lime and bentonite in the proportion of 2 pounds of copper phosphate, 2 pounds of bentonite, and 4 pounds of hydrated lime to 50 gallons of water increased the adhesive properties and lessened the phytocidal action.

Recently, it has been suggested that copper phosphate be made in the tank of the spray machine just previous to application, in a manner similar to the usual preparation of Bordeaux mixture. For this purpose one of the sodium or ammonium phosphates is used (usually Na_3PO_4) with copper sulfate, the reaction apparently being

$$2Na_3PO_4 + 3CuSO_4 \rightarrow Cu_3(PO_4)_2 + 2Na_2SO_4.$$

If one of the sodium acid phosphates is used, calcium hydroxide is added to neutralize the sulfuric acid formed. The precipitated copper phosphate is gelatinous in nature, and adheres well to plant surfaces. Insufficient work on the compound has been reported as yet to justify any conclusions as to its usefulness.

Copper Ammonium Silicate. This material, which has been sold as a fungicide for several years, was developed by Sessions[20] in 1936. Chemically it appears to be a complex combination, made by allowing copper sulfate to react with a mixture of 5 parts of sodium silicate and 1 part of commercial ammonium hydroxide. The copper in the complex is apparently held very firmly, and in this way injury due to soluble copper is kept at a minimum.

Copper Zeolite. A material of somewhat similar constitution to that described above was introduced by Adams and Nikitin[21] in 1935, and has been placed on the market. This material is apparently a complex copper alumino-silicate, and may be prepared from sodium silicate, sodium aluminate (or aluminum sulfate), and copper sulfate. The preparation has been described in detail by Nikitin.[22] This material has the same advantages mentioned above, due to the physico-chemical adsorption of the copper in the silicate complex.

Copper Oxides. Two copper oxides are known to exist: the cuprous oxide, Cu_2O, red in color when viewed in large particles; and cupric oxide, CuO, which is black.

The more highly oxidized form, cupric oxide, has been suggested as the active principle in Bordeaux mixture, although this statement is to be doubted. Marsh, Martin, and Munson,[23] in tests of a series of copper compounds against potato blight (*Phytophthora infestans* (Mont. de Bary)), found that cupric oxide, while inferior in tenacity to Bordeaux mixture, was relatively effective against this particular pathogen. Horsfall, Marsh, and Martin,[24] however, in a later paper found that the fungicidal value of either cupric or cuprous oxide was dependent upon the method of manufacture and particle size, and that the cuprous oxide was more efficient than the cupric form. Although, as will be shown, considerable work has been done with cuprous oxide, less is known of cupric oxide, and it is not used as a fungicide at the present time.

Cuprous oxide was first used as a seed treatment against the damping-off organism *Pythium ultimum* (Tow.).[25] For this purpose it has been found to be an efficient fungicide. It is applied to the seeds as a dust before planting and has considerable power of adherence to the smooth-coated seeds. Horsfall [24, 25] has been active in the development of cuprous oxide for a number of years. In a recent paper, Heuberger and Horsfall [26] have made a study of the color of cuprous oxide in relation to its fungicidal value. It was found that the colors ranged from red through yellow and orange to green, and that the presence of varying amounts of cupric oxide results in various shades of brown. It was found that the color of the pure cuprous oxide was a function of the particle size, the smaller particles having a decidedly yellow color. The range of color and particle size was from 2.57μ for the red colored particles through orange to yellow at about 0.94μ mean particle diameter. Both the direct fungicidal value and the value as a protective seed treatment varied with the particle size; the smaller the particles the more efficient they appeared to be. Because the less efficient cupric oxide is also darker in color, an estimation of the relative value of cuprous oxides on the basis of color is possible. A yellow preparation of cuprous oxide containing a wetting agent is now on the market for use as a fungicide spray. It has been found by Heuberger and Horsfall [27] to adhere well to plant surfaces and to offer a good degree of fungicidal protection without any considerable injury to the plants. In the

field it is usually applied at the rate of 3 pounds per 100 gallons, and is compatible with most spray materials except lime sulfur.

Basic Copper Carbonate. This compound occurs naturally as the mineral *malachite*, $Cu(OH)_2CuCO_3$. Chemically this is the same as verdigris, formed on copper exposed to the air. The basic carbonate *chessylite*, $Cu(OH)_2(CuCO_3)_2$, also occurs in certain parts of the world. The basic carbonate malachite is now used rather widely as a seed treatment, particularly on wheat for the control of bunt (*Tilletia tritici*).

Historically, copper carbonate was first used as a smut fungicide by von Tubeuf [28] in 1902, but was not widely adopted until after the work of Darnell-Smith [29] in 1917.

Copper carbonate is manufactured commercially from copper sulfate and sodium carbonate. It is a greenish amorphous powder, and, according to Briggs and Mackie,[28] should contain from 51 to 54 per cent of $CuCO_3$, and 39 to 42 per cent of $Cu(OH)_2$. The combination, $Cu(OH)_2CuCO_3$, should comprise about 94 per cent of any material used as a fungicide dust for seed treatments. Copper carbonate is usually applied to the seed at the rate of approximately two ounces per bushel of seed. The seed and dry fungicide must be intimately mixed, best accomplished by the use of a rotating chamber or drum. As copper carbonate is irritating to the lungs and throat, it is advisable to use a mask when working with it.

Copper carbonate as a seed fungicide has been found [28] to be slightly less effective than copper sulfate or formaldehyde in solution, but it has the advantage (1) of not affecting germination, (2) permitting the storage of the treated grain for considerable periods after treatment, as well as (3) much greater ease of treatment.

Copper Sulfate (bluestone, blue vitriol)—$CuSO_4 \cdot 5H_2O$. Copper sulfate is usually sold in the form of the pentahydrate, $CuSO_4 \cdot 5H_2O$, although in recent years another form has appeared on the market. This is the monohydrate, $CuSO_4 \cdot H_2O$. As the latter compound contains more copper per unit of weight than the pentahydrate, less is required. One pound of the pentahydrate is equivalent in copper content to 0.72 pound of the monohydrate and to 0.65 pound of the water-free salt.

Copper sulfate has been mentioned previously as having been used to treat posts and ties in vineyards prior to the discovery of

Bordeaux mixture. It was also one of the first of the fungicides used for treating seeds, particularly wheat, against bunt and stinking smut. For this purpose it was first used by immersing the seed in a large container filled with a dilute solution of copper sulfate. Later the seed was piled in a heap, sprinkled with the copper sulfate solution, and thoroughly mixed. Aside from the inconvenience of either of these methods, the treatment invariably decreased the percentage of germination, even though the seed was planted soon after treatment. Application of lime either with or following the copper sulfate treatment has been found to prevent the seed injury to a certain extent. Dry powdered copper sulfate was used by Mackie and Briggs [28] as a seed treatment, both with and without lime. These authors found that, although it was more difficult to use due to its tendency to lump, copper sulfate was almost equal to basic copper carbonate as a dust for seed treatment. The carbonate, however, was to be preferred.

As a spray, the phytocidal properties of copper sulfate even in dilute solutions do not permit its use on living plants.

Miscellaneous Copper Compounds. Since the discovery of the funcigidal properties of copper, numerous copper compounds have been suggested. One group, the copper soaps, or salts of organic acids have found some use. Copper oleate, for example, is used to treat cordage and rope for purposes of preservation and protection. Copper stearate has been tested as a fungicide by Wormald and Wormald,[30] and de Ong [31] has reported the use of copper "resinate," said to have the formula $Cu(C_{20}H_{29}O_2)_2$, dissolved in pine oil and applied as an emulsion. Hamilton [32] has found that cuprous cyanide, CuCN, possessed fungicidal properties, although it caused injury to plants.

Copper acetates have been used as fungicides in France for a number of years, and Butler and Smith [33] have, after considerable investigation, recommended these compounds as spray materials. They have the advantage of leaving a much less noticeable deposit than Bordeaux mixture. Miller [34] has tested the following copper compounds against walnut blight (*Phytomonas juglandis* Pierce): copper acetonate, zinc ammoniacal copper silicate, and copper oxalate. Of these, copper oxalate gave good control of the disease.

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CHAPTER XI

MERCURY COMPOUNDS AND MISCELLANEOUS FUNGICIDES

Certain pathogens are transported and perpetuated by being distributed on the seeds of the plant serving as host. An excellent example of such an organism is the smut of wheat. Other pathogens are widely distributed in most soils, and attack the young seedling at, or shortly after, germination, as for example the "damping-off" organism. Certain fungicides may be applied to the seeds to eradicate those organisms already present, or to serve as a protection for the plant for a limited period after germination. Three compounds of copper, the sulfate, the basic carbonate, and cuprous oxide, have already been mentioned as seed treatments; these are widely used, but recently a group of compounds containing mercury has found rather extensive use as seed-treating agents. Formaldehyde is also used to a considerable extent for seed treatment.

Mercuric Chloride (Corrosive Sublimate)—$HgCl_2$. This compound, also called bichloride of mercury, was first used as a fungicide by Kellerman and Swingle [1] in 1890, who treated wheat with the compound. These authors did not find it particularly effective in the control of stinking smut (*Tilletia foetans* or *T. Tritici*) on wheat. It has since found considerable use as a means of control of Fusarium. It is interesting to note that when used against this disease, the salt not only destroys the pathogen on the exterior of the seed, but those in the interior of the kernel as well.

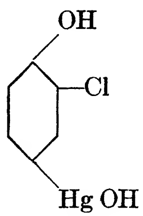
Mercuric chloride has been applied to seeds both in the dry state and in solution. It has been used rather extensively to treat seed potatoes against scab. For this purpose it has been recommended that a 1–500 solution of mercuric chloride in one per cent hydrochloric acid be used to treat the tubers.[2] As an insecticide it is used (in solution) to control earthworms in lawns and golf greens, and as a means of controlling root maggots, such as those attacking cabbages. For this latter purpose it is being gradually replaced by mercurous chloride (calomel), HgCl. The mercurous

salt is relatively insoluble, and is not so highly toxic to living organisms as the mercuric salt.

ORGANIC MERCURIALS

While it was early learned that mercury was a powerful disinfectant and fungicide, the highly toxic nature of its salts (except calomel) led to a search for derivatives which would be specifically toxic for the lower organisms. The organic mercurial compounds have been thoroughly investigated in this connection, and certain of these are now used as fungicides, particularly as seed treatments. The chemistry of organic mercury compounds has been discussed at length in a book by Whitmore.[3]

Hydroxymercurichlorophenol. A compound of this type was first marketed by Bayer in Germany in 1915. Although this substance, sold as "Uspulun," was used in solution or suspension, it was employed rather widely as a seed treatment in Europe. In 1920 a similar product, called "Semesan," was introduced in this country. This apparently is p-hydroxymercuri-o-chlorophenol



and is manufactured by heating o-chlorophenol with mercuric oxide or mercuric salts. It is insoluble in water and common solvents, but is soluble in alkalies and acids giving salts. This compound, alone or in combination with other organo-mercury compounds, is also present in "Nu-Green," "New Improved Semesan Bel," and "Special Semesan."

These materials are used for treating vegetable and flower seeds, seed potatoes, and against "brown patch" (caused by *Rhizoctonia Solani*) and similar diseases of grasses.

Hydroxymercuricnitrophenol. This substance, probably having the hydroxymercuric group in the ortho position, is prepared from nitrophenol and mercuric salts by direct reaction. It is a constituent of "New Improved Semesan Bel" (with hydroxymercuri-

chlorophenol mentioned above). This mixture is sold as a disinfectant for seed potatoes.

Hydroxymercuricresol. Prepared from p-cresol and mercuric acetate, this compound (probably as the sodium salt) is present in "Special Semesan," combined with hydroxymercurichlorophenol. This combination is used to control "brown patch" of grasses.

Ethyl Mercuric Chloride—C_2H_5HgCl. This compound occurs in silvery, iridescent leaflets, and is practically insoluble in water, although slightly soluble in ether, and readily soluble in hot alcohol. The melting point is 192.5° C., but it sublimes easily even at relatively low temperature. It may be prepared in a number of ways, such as the reaction between zinc diethyl and mercuric chloride, or from mercury diethyl and mercuric chloride.

As a fungicide for treating seeds, ethyl mercuric chloride is applied at 2 per cent strength ("Ceresan"), and is particularly recommended for treating cotton, pea and flax seeds. As a liquid dip, it is also recommended for treating certain flower bulbs to prevent basal rot.

Ethyl Mercuric Phosphate. According to Whitmore,[3] this compound is obtained as a thick mass soluble in water by treating a dilute alcoholic solution of ethyl mercuric chloride with silver phosphate. It is an ingredient of two seed disinfectants, "New Improved Ceresan" and "New Improved Semesan Jr.," the former being recommended for treating wheat, oats and rye, and the latter for seed corn.

Miscellaneous Organic Mercury Compounds. While the foregoing organic mercury compounds apparently represent those at present available commercially for use as seed treatments, others have been used with some degree of success in the past. Mention should be made of phenyl mercuric acetate, tolyl mercuric acetate, cresyl mercuric cyanide or iodide, and various methyl mercuric derivatives. Inasmuch as most of this group of compounds have been replaced by those mentioned earlier, it is to be supposed that these more recently developed compounds have certain advantages over those originally sold for the purpose.

Chemistry of the Organic Mercury Compounds. Inasmuch as this group of seed disinfectants has been developed by private interests, first by the I. G. Farbenindustrie A. G. in Germany, and later by English and American firms (E. I. du Pont de Nemours,

later Bayer-Semesan Co., in this country), little is known of the details either of their manufacture or their exact chemical constitution.

In general, however, it is apparent that the compounds mentioned as having value as seed disinfectants may be divided into two general groups, both of which have the general formula $R - Hg - X$. In the first group, R is a cyclic radical, chlorophenol, nitrophenol or cresol, while in the second group, R consists of the simpler, straight chain radicals, such as ethyl or methyl. The portion of the molecule represented by X in the group of cyclic compounds is basic in nature, and these compounds can form salts of the alkali metals. In the second group, X may be an acidic group, such as chloride or phosphate.

Dillon Weston and Booer [4] have reported a study of a large number of compounds of mercury, both inorganic and organic, as seed disinfectants. Their results indicated that in the series of $R - Hg - X$ compounds investigated (in which X was in all cases an acidic radical) the fungicidal power decreased with an increase in the molecular weight of radical R. Certain of the compounds tested showed considerable specificity, and a number of those tested showed little or no practical value. It is important to note that the percentage of mercury in a compound is not an index of its fungicidal efficiency.

MISCELLANEOUS FUNGICIDES

Formaldehyde (formalin)—HCHO. Also called methanal, formaldehyde is a colorless gas at ordinary temperatures (boiling point —21° C.). Commercially it is produced by the oxidation or dehydrogenation of methanol (methyl alcohol) in the presence of a suitable catalyst. It is sold as *formalin*, a 35–40 per cent solution in water and methanol. Formalin, unless purified, contains varying amounts of impurities, such as *formal*, formaldehyde dimethyl acetal, $H_2C(OCH_3)_2$. Formaldehyde has a characteristic penetrating odor, and has the property of forming condensation products with a variety of organic compounds.

As a fungicide, formaldehyde is used principally as a seed and soil disinfectant. For treating seeds it was first suggested in this country by Arthur,[5] who apparently discovered independently the fungicidal properties of formaldehyde in this connection, although

it had been used in Europe previously. Melhus, Gilman, and Kendrick [6] have summarized much of the literature on the use of formaldehyde against potato scab (*Actinomyces scabies*). From their own investigations, these authors found formaldehyde to be an effective agent for the treatment of seed potatoes.

Since treatment of seeds by dry fungicides is usually preferable to liquid treatment, various dry preparations of formaldehyde have been introduced. In these, the formaldehyde is adsorbed upon some inert material, such as bentonite or some organic material, from which it slowly volatilizes on exposure. Such preparations are used for partial sterilization of soil as well.

Zinc Compounds. Various compounds of zinc have been used as fungicides at various times, although none has ever attained wide use. As a seed disinfectant, zinc oxide has been recommended, particularly on the crucifers. It has also been used as a soil disinfectant against damping-off.

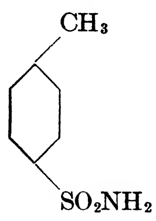
Trials by Kadow [7] with zinc sulfate as a fungicide spray to control peach scab, brown rot, and the like, indicated that this material was not particularly effective, although Young [8] had previously suggested that it be used as a corrective in peach sprays. So-called "zinc Bordeaux" or "zinc lime" has found some use against bacterial spot of peaches (*Bacterium pruni* E. F. Smith). It is similar to Bordeaux mixture, zinc sulfate being used instead of copper sulfate.[9] In this connection, Hurt [10] has suggested the use of zinc hydroxide as a substitute for calcium hydroxide for the prevention of arsenical injury. Against the fire-blight organism, Day [11] has applied relatively concentrated solutions of zinc chloride directly to the infected area on pear and apple trees. Various zinc salts also find considerable use as wood-treating agents to prevent fungus growth. One manufacturer markets a mixture of zinc chloride and sodium dichromate for use as a wood preservative and termite repellent. Due to the value of zinc in certain deficiency diseases of citrus and pecan trees, sprays containing this element may serve a double purpose.

Other Fungicides. For certain specific purposes a wide variety of fungicides has been recommended from time to time. Many of these have not found wide application while others have been suggested too recently for a proper evaluation of their usefulness. Mention should be made of phenothiazine, discussed in Chapter III

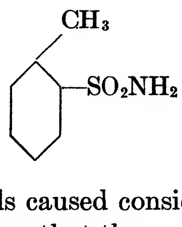
at some length as an insecticide. This compound has been studied by Goldsworthy and Green [12] and others as a fungicide. As in the work on the insecticidal value of phenothiazine, these authors found that the oxidation product phenothiazone, rather than phenothiazine, was the toxic principle involved. According to their tests, phenothiazone at concentrations of several parts per million in aqueous solution was toxic to the conidia of *Sclerotinia fructicola* and *Glomerella cingulata*. Phenothiazine and its oxidation products are receiving further attention from a number of investigators, and it appears that the value of the compound as a fungicide may be greater than as an insecticide.

Benzol (C_6H_6), when vaporized, has been found by McLean et al.[13] and Wolf et al.[14] to be very effective in the control of downy mildew (blue mold) of tobacco (*Peronospora tabacina*). For this purpose the benzol is used as a fumigant. Monochlorobenzene and paradichlorobenzene have also been used in the same way against this organism.

Other compounds have been used against the leaf rust (*Puccinia triticina*) and stripe rust (*P. glumarum*) of wheat, including borax (sodium borate, $Na_2B_4O_7 \cdot 10H_2O$), picric acid (s-trinitrophenol, $C_6H_2(NO_2)_3 \cdot OH$); para-toluene-sulfonylamide,



and ortho-toluene-sulfonylamide,



Although these compounds caused considerable plant injury, they were so remarkably effective that they appear to hold considerable promise.[15]

Furfural has been tested as a fungicide by Flor,[16] and malachite green against downy mildew of onions (*P. destructor*) by McWhorter and Pryor.[17] This last compound, which is a double zinc chloride or oxalate, $(C_{23}H_{25}N_2Cl)_3 \cdot 2ZnCl_2 \cdot 2H_2O$ or $(C_{23}H_{25}N_2)_2 \cdot 3H_2C_2O_4$, was particularly effective when used in combination with cuprous oxide. Another dye, crystal violet, has been used as a fungicide.

Wood and Cellulose Preservatives. The use of wood preservatives, which in reality function mainly as protective fungicides, has increased considerably in the past few years. For this purpose a wide variety of chemical substances has been used. The use of zinc chloride alone and in combination with sodium dichromate in this connection has already been mentioned. A copper sulfate-sodium arsenite mixture has also been used with considerable success. Aqueous solutions of both borax and copper sulfate have been found to be effective. Among the organic compounds which have been suggested for this purpose are ethyl mercury chloride and ethyl mercury phosphate, phenyl mercury oleate, and phenyl mercury nitrate. These substances are particularly useful to prevent fungus sap stains on lumber and millwork. Phenol, cresol, naphthalene, 2-chloro-, tetrachloro- and pentachlorophenols, parachlorometacresol, dinitrophenol, and paranitrophenol have also recently come into use. Other organic compounds found to have some promise as wood preservatives are dichlorodiphenyl oxide, (p-*tert*-butyl-phenoxy) ethanol, p-chlorophenoxyethoxyethyl chloride, and o-nitrodiphenyl, the first three compounds being dissolved in kerosene, the last in benzene. The use of creosote oils has, of course, been practiced for many years.

Protective Fungicides for Fabrics. Furry, Robinson, and Humfeld[18] have studied a large number of chemicals as agents to prevent the growth of mildew on fabrics. Unbleached cotton duck was used as the test fabric, inoculated subsequent to treatment with *Chaetomium globosum* Kunze and incubated. The following treatments gave satisfactory protection:

Miscellaneous organic compounds:

Acetylation using acetic anyhydride, glacial acetic acid, and zinc chloride.

Acetone with formalin.

An alkylated dimethyl benzyl ammonium phosphate alone and followed by methyl acrylate resin.

Substituted phenols:

Salicylanilide applied alone and followed by methyl acrylate resin, not steam-sterilized; an emulsion of salicylanilide with wax and aluminum acetate emulsion.

o-Phenylphenol; 2-chloro-o-phenylphenol; pentachlorophenol.

Sodium pentachlorophenolate alone and followed by borax, cadmium chloride, monobasic lead acetate, or aluminum potassium sulfate.

Thymol with phenyl salicylate.

Chlorothymol applied alone and followed by wax and aluminum acetate emulsion when not steam-sterilized.

Dyes and mordants:

Catechu.

Organometallic compounds and metallic salts of organic acids:

Copper propionyl acetonate.

Copper and zinc naphthenate.

p-Tolyl mercury salicylate.

Phenyl mercury oleate.

Cadmium soap; copper soap.

Inorganic salts:

Cadmium chloride followed by borax.

Copper sulfate and sodium hydroxide; copper sulfate and sodium carbonate; copper sulfate followed by wax and aluminum acetate emulsion when not steam-sterilized.

Sodium sulfide followed by potassium dichromate.

Not all of these compounds which proved effective as mildew preventatives were satisfactory as fabric treatments, some being colored, for example. The list is here reproduced, however, to indicate the range of chemical compounds which have been found useful as protective fungicides for fabrics.

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Part IV

Spray Supplements

and

Residue Removal

CHAPTER XII

SPRAY ADJUVANTS

Wetting, Spreading, Emulsifying, and Adhesive Agents

It has long been observed that liquid spray mixtures did not all behave in the same manner when applied to plant and insect surfaces. The greatest apparent difference was in the character of the films produced. A spray mixture when applied to certain surfaces gave a continuous film, while the same mixture on a different surface was deposited in discrete droplets. Similar differences were also observed with different spray liquids on the same type of surfaces.

The factors which in the main determine the type of deposit of a spray upon plant and insect surfaces are the chemical and physical properties of the spray mixture, and the physical properties of the surface itself. The chemical properties of the spray materials have already been discussed, but so far the physical properties of sprays have not been considered.

WETTING AND SPREADING

A number of writers have discussed the wetting and spreading properties of spray fluids at some length, including Cooper and Nuttall,[1] Hamilton,[2] Moore,[3] Woodman,[4] and O'Kane and associates.[5, 6] Adam,[7] in his recent book, has also discussed surface phenomena in general, and the reader is referred to this or some other standard text on colloid chemistry for a more complete discussion of the subject.

The properties of wetting and spreading may be understood best, perhaps, by the use of a specific example. When a droplet of water is placed upon a surface which it does not wet, such as a piece of paraffin, it assumes a spherical shape. This is caused by the *surface tension* of the water. Surface tension in a liquid is due to molecular cohesion; that is, in the body of the liquid below the surface, the molecules of the liquid have a pronounced attraction for each other. This attraction, because each molecule is surrounded by others, is exerted equally in all directions.

At the surface of a liquid, however, a different situation exists. Here the molecules are subjected to attraction mainly from the liquid phase, this force exerted on these surface molecules causing them to be more closely grouped together, and hence to exhibit different properties from those below the surface. Briefly, a "skin" is formed over the surface of the liquid, and in this "surface skin" the molecules are usually oriented in a rather regular fashion, and are in greater concentration than in the remainder of the liquid. This surface "skin," being under tension, tends to pull the body of liquid which it surrounds into the smallest possible volume for a given surface area, thus resulting (if the drop is not subjected to other forces) in the formation of a sphere.

To return to the drop of water lying on a paraffin surface. Such a drop, as a result of surface tension, is pulled into a spherical shape (more or less deformed, actually by the pull of gravity). This is shown as *A* in figure 19. Spherical globules of liquid are

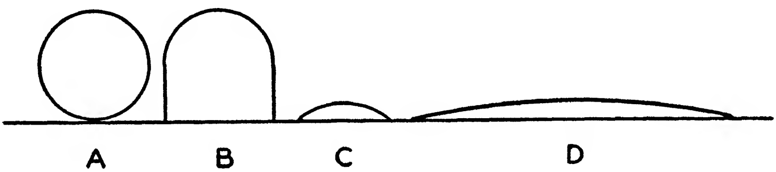

FIG. 19. Droplet forms illustrating different degrees of wetting and spreading.

formed when a liquid is suspended free in space, or when in contact with a surface *which is not wetted by the liquid.* Besides water on paraffin, a familiar example of this phenomenon is a droplet of mercury on a glass plate.

When the liquid wets the surface upon which it is placed, a different situation exists. Here other forces tend to pull the liquid out in a plane along the surface wetted. Here a rather fine distinction must be made between *wetting* and *spreading.* There has been considerable confusion of terms in this case, but it appears that before a liquid can *spread* it must *wet* the surface; hence the one precedes the other in a sense, although the two phenomena are so closely related that the distinction is difficult. Moore [3] speaks of the phenomenon of wetting as a "slight chemical affinity exhibited between liquid and solid."

When a drop of liquid comes in contact with a solid which it really wets, then the course of the subsequent events depends broadly on the magnitude of three forces: the surface tension of the liquid; the apparent surface energy of the solid (which at present cannot be measured); and the interfacial tension between the solid and the liquid. The surface energy of the solid will tend to pull the liquid out into a film with the maximum surface. Opposing this will be the surface tension of the liquid and the interfacial tension. Theoretically, then, if a liquid wets a solid but does not spread upon it, the drop assumes the form shown in figure 19 *B*. Actually, of course, such a condition probably never exists.

When wetting and spreading both take place, the drop of a liquid assumes a form similar to figure 19 *C* and *D*. The extent of the spreading (called by some workers "extension") depends on the equilibrium which is established between the forces mentioned in the previous paragraph; for liquids with very low surface tension and high spreading ability, it is possible to produce a film, the surface of which is practically parallel to the surface upon which the drop is deposited.

A convenient measure of the ability of a liquid to wet and spread upon a given surface is the *contact angle*. This is the angle between the liquid and the solid when equilibrium is reached. Thus, for a liquid on a solid which it does not wet, the angle of contact will be 180°, whereas if the surface is completely wet, the angle of contact will be 0°. Between these two extremes there is partial wetting, and the smaller the contact angle the greater the degree of wetting. Two types of contact angles are usually measured: the advancing contact angle, which may be measured by placing a drop of liquid to be tested upon the surface and measuring the angle at equilibrium, and the receding contact angle which results, for example, when a portion of the drop has been abstracted after it has been placed on the solid. Measurements may be made in a variety of ways.

The performance of a liquid insecticide spray, particularly a contact spray, can be seen to depend to a very large degree on the ability of the spray to spread over the surface to which it is applied. It is obvious, further, that the spreading and wetting properties of a spray liquid may be changed by changing the physical properties, such as the surface tension of the liquid.

It is in this connection that a large number of supplementary materials have been introduced in the insecticide field during the past few years. Those intended to increase the spreading and wetting powers of sprays are often loosely termed "wetting agents," or "spreading agents." Certain of the materials used in this connection are also adhesive agents, a group which will be discussed later. Most of the effective wetting and spreading agents act by lowering the surface tension of water in which they are dissolved. It has been shown by the work of Langmuir,[8] and Harkins, Davies, and Clark,[9] that substances in which there is a long-chain grouping in the molecule combined with a highly water-soluble group are extremely efficient in lowering surface tension in solutions. These authors have further pointed out that at the surface of such solutions a concentration of the active material occurs, according to Gibbs' equation, with an orientation of the long-chain (non-polar) group directed away from the water, and the water-soluble (polar) group of the molecule oriented toward the water. Most of the chemical substances which are used as wetting and spreading agents are so constituted and behave in this manner.

WETTING AND SPREADING AGENTS

Soaps. The chemistry of soaps has been discussed earlier (pp. 126–130) in connection with their use as insecticides. It should be pointed out here, however, that soaps, consisting of a long chain of carbon atoms (the salts of the shorter chain fatty acids show little or no surface activity), a non-polar group coupled with a polar COOH group, are good examples of the type of compound mentioned in the previous paragraph.

The distinction between soap as a spreading agent and as an insecticide is difficult to make, for in most cases it functions as both. Historically, soap has been used in combination with other materials in insecticides for many years. Lodeman[10] cites a recommendation published in 1787 for the use of tobacco and soap as a method of controlling plant lice (aphids). Today nicotine sulfate is ordinarily used in combination with soap against these same insects, indicating that in over a century and a half the change in the method of control has been relatively minor.

Soaps are particularly useful in contact sprays, because they are, as mentioned previously, useful as insecticides in themselves.

Two general types of soap are common, the hard (sodium) soaps and the soft (potassium) soaps. For spraying purposes, the latter are usually preferred, as they are more readily miscible with cold water. Many specific soaps have been used as spreading agents in insecticidal sprays, the cheaper grades being entirely suitable, because for this purpose a pure product is not necessary. The whale- and fish-oil soaps have been widely used with considerable success.

Salts of abietic acid, which is the diterpene carboxylic acid of rosin, have been used as wetting and emulsifying agents. Sodium, potassium, and ammonium oleoabietates are available commercially, and are known as "rosin soaps." Unless sulfonated, the abietates react with hard waters as do the other soaps, and thus are subject to the same limitations. Algin soaps, formed from the hydroxy aldehyde acids present in seaweed, have also been used as wetting agents.

One of the disadvantages to the use of soaps is the ease with which the calcium and magnesium soaps are formed with hard water, the soap almost invariably reacting to form curds of insoluble calcium and magnesium soaps which, by their insoluble nature, are worthless as spreading agents. This fact also precludes the use of soaps as spreaders for spray mixtures containing lime. Roark [11] has pointed out the incompatibility of soap with pyrethrum preparations because of the hydrolysis of the pyrethrins brought about by the alkali of the soap. Ginsburg [12] has studied the reaction between various soaps and lead arsenate. He found that, with the oleates, salts of strong bases (sodium and potassium) liberated more soluble arsenic than those of weak bases (ammonium and triethanolamine).

Saponins. The saponins are glucosides occurring in several species of plants, such as soapwort (*Saponaria officinalis*). The saponins are hydrolyzed by mineral acids to yield sugars, such as glucose, galactose, and arabinose, together with "sapogenins" of unknown and complex structure. The saponins form colloidal suspensions with water, are characterized by their ability to foam readily, and are quite effective detergents, because they greatly reduce surface tension. Crude preparations of saponins have been used as spreading and wetting agents in connection with insecticide sprays, but at present saponins are rarely used for this purpose.

The saponins possess considerable physiological action, and may be useful in themselves as insecticides.

Gelatin. A protein preparation of animal origin, gelatin was first used as an adjuvant for sprays by David [13] in 1885 with Bordeaux mixture. Glue, prepared from similar sources, has similar properties and has also been used in sprays. While these materials have the property of lowering surface tension, they are usually used as adhesives.

Casein and Casein Preparations. The use of milk to lower the surface tension of sprays was recommended at an early date, and Lodeman [10] in 1896 stated that condensed or sour milk was more effective than sweet milk for this purpose. Later, when dried milk products became available, dried skimmed milk was used in sprays, both to increase the wetting and spreading ability, but particularly as an adhesive agent.

The surface activity of milk preparations depends upon the presence of proteins, of which casein is present in the largest quantities, although the "soluble" or whey proteins probably act in a similar manner. Casein, used either alone or in combination with lime or some other inorganic salts, was first suggested by Vermorel and Dantony [14, 15] in 1913.

Although precipitated casein is insoluble in water, the addition of alkali makes it disperse readily. Lime is usually used for this purpose, and "lime casein" or "calcium caseinate" preparations have been widely used as spreading, wetting and adhesive agents. The low cost of such preparations makes them widely available and, unlike the soaps, they may be used in hard waters and in the presence of large quantities of lime. "Calcium caseinate" on the market is probably a mechanical mixture of calcium hydroxide and casein in the proportion 3 : 1.

Flour. Like gelatin and casein, the proteins in wheat flour will also act as spreading, wetting, and adhesive agents. Because of its cheapness, flour has been used to a considerable extent for this purpose in the past.

Sulfite Lye—(lignin pitch, sulfite liquor). This material, a by-product of the paper industry, contains the soluble portions of wood pulp, including the lignins and other carbohydrates, together with certain inorganic salts. When concentrated, it is sold either as a viscous brown liquid with a specific gravity of about 1.3, or

as a dry powder, the latter being more economical to transport. Chemically, little is known of the constitution of the material, although lignosulfonic acids have been identified in it.

Sulfite lye has pronounced surface-active properties, due probably to the combination of the lignin molecules with the sulfonic acid. Martin [16] first suggested this material as a spreading and wetting agent for sprays, and because of its cheapness it has found considerable use. Evans and Martin [17] have shown that sulfite lye was particularly valuable as a wetting agent, rather than as a spreader.

Proprietary Wetting Agents. Within the past few years a large number of organic wetting and spreading agents have appeared on the market. Many of these were first used as wetting-out and degumming agents in the textile industry, and some have found considerable use as supplements for insecticides and fungicides. A considerable number have also been used to facilitate the removal of spray residues from fruits after harvesting.

As a group, these materials are organic in nature, and are characterized by a relatively high wetting and spreading activity; a small amount of the material suffices to lower the surface tension of a relatively large volume of water. Most of the group possess the further advantage of being non-reactive with the calcium and magnesium salts present in hard waters, and mainly for this reason have been used to replace soaps in sprays.

Many of the compounds on the market are mixtures of several chemical compounds. A number of manufacturers are reluctant to divulge the chemical composition of their product. Consequently, complete classification is difficult. The information given in the discussion which follows has been taken mainly from lists published by Cupples.[18, 19] Because trade names are often transitory, the reader is cautioned to consult the manufacturers for the exact chemical composition of any of the commercial materials mentioned. The list of materials given is by no means complete, only representative compounds being listed.

Long Chain Alcohols. Long chain alcohols, formula R—OH, where *R* is a fatty alkyl group, have found considerable use as wetting agents, although they are ordinarily insoluble in water. They may be made from the corresponding fatty acids or from petroleum. Examples of this type of compound are lauryl alcohol

(1, dodecanol), $CH_3(CH_2)_{11}OH$ in *Lorol;* oleyl alcohol (octadecen-9-ol-1), $CH_3(CH_2)_7CH = CH(CH_2)_8OH$ in *Avitex* and *Ocenol*, and stearyl alcohol (octadecanol), $CH_3(CH_2)_{17}OH$ in *Avitex* and *Homogenol W W*.

Alcohol and Acid Sulfates and Derivatives. The most common materials belonging to this class are the salts of sulfated alcohols. Roark [20] has pointed out the confusion which exists in certain quarters regarding the terms *sulfated* and *sulfonated.* The former compounds are esters of sulfuric acid, and are more properly called alkyl sulfates if the alcohol belongs to the series $C_nH_{2n+2}O$, or alkenyl sulfates if the alcohol belongs to the series $C_nH_{2n}O$, are made by treating the alcohols with sulfuric acid, chlorosulfonic acid, or sulfur trioxide under carefully controlled conditions. The sulfonates, on the other hand, contain the radical SO_3H. These may be formed if the temperature of sulfation is too high.

The sulfates of the fatty alcohols are commonly used in the form of the sodium salts, with the generalized formula $R - SO_4Na$. Examples of such compounds are sodium oleyl sulfate in *Duponol L S*, and *Gardinol L S* and sodium lauryl sulfate in *Dreft*, *Duponol M E* and *Orvus W A*. *Grasselli Spreader-Sticker* contains sodium oleyl sulfate and a synthetic resinous sticker. *Tergitol 4* and *Tergitol 7* contain the sodium sulfate of a higher synthetic secondary alcohol. The sodium salts of sulfated fatty acid amides with the formula $R - CONHC_2H_4SO_4Na$, and the esters of sulfated fatty acids, $R - COOC_2H_4SO_4Na$, are also used as wetting agents. Among the older materials used as wetting agents should be mentioned *Turkey red oil*, produced by the sulfation of castor oil. This contains the ammonium salt of ricinoleic sulfuric acid ester.

Sulfonated Aliphatic Derivatives. Of the alkyl sulfonates, the *Igepon* group is of considerable importance. According to Roark,[20] *Igepon A* is formed by the action of isethionic acid (hydroxyethane sulfonic acid, $HOCH_2CH_2SO_3H$) or its salt upon oleic acid or its derivatives. The formula for *Igepon A* is

$$CH_3(CH_2)_7CH = CH(CH_2)_7COOCH_2CH_2SO_3Na$$

This compound cannot be used with alkalies, however, as they split the molecule at the carboxyl group with the formation of a soap. To correct this difficulty, *Igepon T* was developed, which stands up better in both alkaline and acid solutions. The formula

for this material is

$$CH_3(CH_2)_7CH = CH(CH_2)_7CONHCH_2CH_2SO_3Na$$

The *Arctic Syntex* groups are similar in composition to the *Igepons*. In general, the sulfonation of a secondary alcohol or a dibasic acid produces a more surface-active compound than the straight-chain alcohols and acids. Numerous such compounds are on the market: *Aerosol O T*, for example, is a dioctyl ester of sodium sulfo succinate. Sulfonated ethers are the active principles in *Triton 720* and *Triton 812*.

At this point should be mentioned the large group of sulfonated petroleum products. These compounds, which are sometimes termed "mahogany soaps" are formed as by-products in the refinement of petroleum oils, particularly in the production of "white oils." In this process the oils are subjected to drastic sulfonation, and the sulfonated residue separated as a sludge from the oil. When these sludges are treated with an alkali the salts are formed. Usually sodium carbonate is added, and the resulting sodium salts are soluble in water. Due to the complex mixture of chemical compounds present in the treated petroleum, it is not possible to assign formulas to the sulfonated materials produced. It is said, however, that the average number of carbon atoms per molecule of these compounds is 16. *Ultrawet* and *Penetrol* are examples of this class of material. Martin [21] has classified the petroleum sulfonates as follows:

1. Calcium γ-sulfonates, isolated from the residue remaining from the refinement of lubricating oil by treatment with lime. These calcium-γ-sulfonates are soluble in water and ether and have excellent spreading properties and are not affected by the usual materials used in spray mixtures.

2. The sodium-β-sulfonates, which are extracted from petroleum oils after acid treatment. These are similar to the γ-sulfonates and are separated from them by the solubility of the calcium salts; the calcium salts of the β-sulfonates being soluble in ether but insoluble in water. These preparations are excellent spreaders, but react with lime and copper sulfate, so that their use is more limited than the γ-sulfonates. These β-sulfonates, however, appear to be particularly adapted to the preparation of miscible oils.

3. Products prepared by the sulfonation of oxidized petroleum oils. One of these, *Penetrol,* has been on the market for some time. These materials are compatible with lime and copper salts and possess good spreading powers.

The classification of the β- and γ-sulfonates is based on an earlier paper by von Pilat, Sereda, and Szankowski,[22] and it is to be noted that certain of the compounds mentioned elsewhere in this chapter are derived from petroleum; this is true of the naphthenates and others. A recent book by Burton and Robertstraw [23] discusses the sulfated oils in considerable detail, and includes a number of useful analytical procedures.

Sulfonated Aromatic and Mixed Alkylaryl Derivatives. A number of the proprietary wetting agents are sulfonated aromatic derivatives. A few examples of such compounds are sodium m-nitrobenzenesulfonate, sold as *Albatex BD,* and sodium naphthenic sulfonate, *Emulsifier W-763-A.* Mixed alkyl aryl derivatives, such as sodium alkylnaphthalenesulfonate, are present in *Alkanol HG* and the sodium disulfonate of dibutylphenylphenol in *Aresklene.*

Esters of Fatty Acids. A small group of wetting agents comprising the esters of various fatty acids with the hexahydric alcohols mannitol and sorbitol are of interest because they possess considerable insecticidal value in addition to their value as wetting agents. Sorbitan monolaurate, $C_6H_8O(OH)_3(OCOC_{11}H_{23})$, *Atlas G-759,* the ricinoleic acid ester of sorbitol, *Atlas G-650,* the monostearates of sorbitan and mannitan, and mannitan monolaurate have been prepared. This last compound, $C_6H_8(OH)_3(OCOC_{11}H_{23})$, sold as *Atlas G-904* as a wetting agent and *NNO* as an insecticide, appears to have considerable toxicity to certain insects.

Miscellaneous Materials Used as Wetting Agents. In addition to the organic materials already mentioned, a variety of substances have been used as wetting agents in combination with insecticides and fungicides. Mention should be made of the pine oils, composed mainly of terpineol, fenchyl alcohol, the terpene hydrocarbons, and borneol; powdered locust bean gum (*Lupogum*); and soybean lecithin, which contains organic phosphatides. Quaternary ammonium salts have also found some use.

Clays and Related Materials. While clays in various forms such as fuller's earth, china clay, kaolin, and bentonite are mainly

used as adhesive agents and emulsifiers, the colloidal properties of such materials may affect the spreading action of a liquid in which they are suspended. As detergents, clays have been used for many centuries, antedating soap, which was not introduced until about the first century A.D., and did not become widely used for several centuries thereafter. The most widely used material of this type in the insecticide-fungicide field is bentonite, a natural clay of volcanic origin. The active principle of clays is hydrated aluminum silicate which has the property of taking up large volumes of water, forming a colloidal gel. Bentonite is sometimes processed with magnesia to render it more readily dispersible in water.

EMULSIONS AND EMULSIFYING AGENTS

Oils and other liquid insecticides and fungicides not miscible with water are usually applied in the form of emulsions. An emulsion is defined as a minute division of one fluid in another in which it does not mix. The liquid in which another is truly suspended is termed the continuous phase; the other, or suspended liquid, the disperse phase. From this it is obvious that for any given pair of liquids, two types of emulsions are possible. In the case of oil and water, for example, it is possible to have either an oil-in-water or a water-in-oil emulsion.

It is usually very difficult to produce an emulsion consisting of two pure materials. Therefore, a third substance, an emulsifier, is added. The choice of emulsifier ordinarily determines the type of emulsion obtained, certain emulsifiers producing the oil/water type, others the water/oil type. Emulsions are stable when the interfacial tension between the phases is low, so that any substance which lowers the surface (interfacial) tension of water will tend to stabilize a water emulsion. Thus the statements already made in the earlier part of this chapter regarding surface tension-active substances apply here as well. In fact, most wetting and spreading agents previously mentioned will function as emulsifying agents.

The most common emulsions used as insecticides and fungicides are those containing water and a petroleum or tar oil. These may be made from the raw materials—for example, oil, emulsifier and water—in the spray tank. This is the so-called "tank-mix"

method, and is quite successful, provided the spraying apparatus is provided with an efficient agitator. Martin [24] has proposed a modification of this procedure which he calls the "two solution method," in which a soap is formed by alkali and a fatty acid at the same time the tar or petroleum oil is emulsified.

The second common method of preparing emulsions for insecticidal purposes is by the use of stock emulsions, or "miscible" oils. The stock emulsions on the market are prepared mixtures of oil, emulsifier (with or without an added stabilizer), and a small amount of water. These stock emulsions usually contain approximately 80 per cent of oil, the balance inert ingredients, and are prepared in most cases by passing the finished product through a colloid mill or homogenizer. The miscible oils contain the emulsifier dissolved in the oil. Both types require only to be added to water with mild agitation to produce a satisfactory emulsion, and are convenient to use. The chief disadvantage of the stock emulsions lies in the ease with which the constituents may become separated on standing or freezing.

A number of workers have investigated the factors which affect the deposition of oil from oil emulsion sprays. Hoskins and associates,[25, 26, 27] and Smith [28] in particular, have investigated a number of phases of the problem, and have confirmed the earlier work of de Ong et al.[29] showing that as far as deposit was concerned a "quick breaking" emulsion was better than one more stable.

As mentioned before, most of the materials discussed as spreading and wetting agents act as emulsifiers as well. Solids which have an affinity for one of the phases of the emulsion and thus tend to collect at the interface are also used in this connection. These include the proteinaceous materials, such as dried milk preparations, liquid milk, either fresh or sour, skimmed or condensed, dried blood, tankage, and gelatin. Bordeaux mixture is a relatively efficient emulsifier and the clays, particularly bentonites, are widely used. In addition, other supplementary materials are sometimes added to emulsions to stabilize them, some of them being mutual solvents such as cresols, phenols, or amyl alcohol. Eddy [30] gives a number of formulas for preparing miscible oils.

Inverted or "Dynamite" Sprays. The discussion of emulsions would not be complete without mention of the inverted type of

spray mixture developed at the Washington State College by Marshall and associates.[31, 32] In these mixtures, the suspended solid (for example, lead arsenate) initially wetted by water becomes wetted by oil prior to, or at the moment of, impact upon a sprayed surface. The inversion of an arsenical spray mixture requires the addition of some substance such as a fatty acid, a soap, or other fatty acid compound to promote oil-wetting of the arsenical, which is normally preferentially wetted by water. The most satisfactory soaps were found to be the oleates of mono- or triethanolamine or ammonia. A typical formula for an inverted mixture is composed of two separate solutions: the first consisting of 1 part high grade oleic acid plus 19 parts of raw summer petroleum oil, thoroughly mixed; the second, containing the base, consists of 1 part of monoethanolamine or 25 per cent ammonia plus 12 parts of water. For 100 gallons of spray, 1/2 pint of the second solution is stirred into 1 gallon of water, and 2 quarts of the first solution added with thorough agitation. To a large volume of water in the spray tank are added 3 pounds of lead arsenate, and when the tank is nearly full, the oil emulsion is added. Flocculation of the lead arsenate occurs, and the spray may be applied within a few seconds.

The chief advantage of inverted or "dynamite" sprays as they are sometimes called lies in the fact that considerably greater deposits of lead arsenate (or other suspended solid) may be obtained from them than from ordinary spray mixtures. With a non-inverted mixture, once the fruit has been wetted, no more suspended solids can be made to adhere, while with the inverted mixture, the oil and solid constituents remain on the fruit while the water drips to the ground.

Within the past few years, proprietary mixtures have been placed on the market which, when mixed with spray suspensions, are said to produce an inverted type of mixture. There has not been sufficient work reported with these to permit judgment as to their efficacy.

ADHESIVE OR STICKING AGENTS

Adhesive agents, or stickers, as the name implies, are those substances which function to increase the retention or tenacity of spray deposits. Certain of the materials used as spreading and

wetting agents may also function as adhesives; this is particularly true of the proteinaceous materials, such as milk products, flour, gelatine, and blood albumin, mentioned previously. These are hydrophylic colloids and apparently form a very tenacious coating upon the plant surfaces when dried. Similar in action, although different chemically, are the bentonites and other clays.

It is the oils, however, that constitute the most important group of adhesive agents. Hood [33] and many other later investigators have reported the efficiency of fish oils as adhesives. On the surface of the apple fruit, for instance, and to a lesser extent on leaves in general, these oils tend to form an intimate union with the surface coatings, and thus adhere very strongly. Whether this union is physical or chemical has not been determined. Since these oils are usually applied in the form of emulsions, they may possibly increase the amount of suspended solid retained by mechanically enmeshing the suspended particles in a "varnish-like" film.

DEFLOCCULATING AGENTS

Materials which retard sedimentation of suspended insecticides are sometimes incorporated in spray mixtures to increase the homogeneity of the suspension. The protein materials mentioned previously—glue, gelatin, milk products, and various gums—are used for this purpose. Certain brands of lead arsenate on the market contain a small percentage of deflocculator as sold. The tendency toward the use of more finely divided solids as insecticides has made the use of deflocculators unnecessary in many cases, however.

SYNERGISTS

The use of synergists, materials which may or may not be toxic in themselves, but which increase the insecticidal effectiveness of other toxic materials, has recently received considerable attention. Sesame oil and isobutyl undecylenamide have been found to increase the insecticidal value of pyrethrins when mixed with them in solution in kerosene. Certain gums may function to increase the insecticidal value of nicotine, and it is possible that certain of the proprietary wetting and spreading agents may act as synergists with rotenone, nicotine, and pyrethrum. Much further work must be done, however, before the mechanism of action and the value of these materials are established.

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CHAPTER XIII

SPRAY RESIDUE REMOVAL

Because the spray residues remaining on edible fruits and vegetables are in many cases ingested by the consumers of these products, and because many of the insecticides commonly used are toxic to man as well as insects, there has been considerable concern on the part of public health authorities. The problem apparently first arose soon after the extensive adoption of the members of the arsenic group as insecticides. As early as 1880, Cook [1] reported no arsenic on apples sprayed with Paris green and London purple, although subsequent work by Kirkland,[2] O'Gara,[3] and many others indicated that arsenic in measurable amounts was present on fruits after spraying, particularly when the newly introduced lead arsenate had been applied as an insecticide.

Historically important in this connection is the careful study made by O'Kane, Hadley, and Osgood [4] on the quantity and toxicity of arsenic residues on fruits and foliage following applications of lead arsenate. These authors concluded that there was sufficient arsenic on fruits, vegetables, and vegetation under fruit trees to cause potential injurious effects on human beings and livestock.

In England, due to the poisoning of several thousand persons from drinking beer containing arsenic, regulations were early enforced controlling the amount of arsenic permitted in foodstuffs. The maximum amount permitted was set by the Royal Commission on Arsenical Poisoning at 0.01 grain of arsenic trioxide per pound of food, equal to 1.43 parts per million. But this limit was apparently not rigidly enforced and it was not until 1925, following the reported illness of several persons after eating American apples, that the English authorities began rejecting shipments of apples found to be above the legal tolerance. Just prior to this time, the United States Department of Agriculture had anticipated such a move by surveying the residue situation in the principal apple-growing areas of the country. Early in 1927, the Food and Drug Administration set a legal tolerance of 0.025 grain of arsenic tri-

oxide per pound of fruit. This limit was subsequently lowered to 0.020 grain in 1928; 0.017 grain in 1929; 0.015 grain in 1930; 0.012 grain in 1931; and finally to the British or "world tolerance" of 0.01 grain (1.43 p.p.m.) in 1932.

A board of experts meeting at the request of the U. S. D. A. in 1927 reported that in their opinion lead residues were more significant from the point of view of public health than arsenic, because of the fact that lead appeared to be a cumulative poison. The gradual lowering of the arsenic tolerance mentioned in the previous paragraph was an attempt to reduce the amount of lead residues indirectly, by regulation of the arsenic content, because it was presumed that the ratio of lead to arsenic in spray deposits was the same as in the applied lead arsenate (approximately 2 to 1). It soon became apparent, however, that such an indirect control was not satisfactory, and in 1933 a limit was set of 0.02 grain (originally set at 0.014 grain) of lead per pound of fruit. The same announcement set a limit of 0.01 grain of fluorine per pound.

Because on most fruits the ratio of lead to arsenic was greater than 2 : 1, lead thus became the limiting factor; that is, in order to meet the lead tolerance of 0.02 grain per pound, most of the fruit came below the arsenic tolerance of 0.01 grain per pound. The tolerance for lead in 1940 was raised to 0.050 grain per pound. The 1940 tolerance for arsenic (as As_2O_3) was 0.025 grain per pound, fluorine 0.02 grain per pound. To meet this situation growers have thus been faced with four alternatives: (1) To apply no protective sprays or dusts, and run the risk of partial or complete loss of crop through insect and disease attack; (2) To apply the toxic materials in relatively small amounts, so that by harvest time the amount of residue will be below the legal limit; (3) To apply preparations toxic to insects and diseases but non-toxic to higher animals; or (4) To apply toxicants in sufficient quantities to control the plant pests and, at some time prior to marketing, to remove the poisonous residue. With valuable crops of vegetables in which the cost of the application is small in relation to the value of the crop, materials such as rotenone or pyrethrum are now widely used (method 3). With fruit crops, however, if sprays are applied, the grower usually restricts the number of applications to a minimum and in addition removes the residue before marketing (combination of methods 2 and 4).

METHODS USED TO REMOVE RESIDUES

Dry Wiping. The first attempts at residue removal from fruits were by the obvious means of mechanical wiping. In fact, according to Frisbie,[5] the field force of the Bureau of Chemistry, in the early days charged with the enforcement of the Food and Drugs Act, was instructed to require shippers of apples to remove visible residues by wiping, so confident were the authorities that if the recommended spray schedules were followed, thorough wiping of the fruit would constitute a sufficient safeguard. Spray adjuvants, such as casein, oils, and other sticking agents soon came into common use, nevertheless, and freedom from visible residue was soon found to be no guarantee of freedom from measurable amounts of toxicants. Various mechanical dry wiping machines were introduced and used to a certain extent, although the work of Heald, Neller, Overley, and Dana,[6] and others indicated that in many cases the wiped fruit showed a slightly higher residue than the unwiped, probably because of the accumulation of the spray deposit on the brushes or cloths used in the machines. Of the many trials of dry wiping machines, none indicated a satisfactory reduction in the deposit on the surface of the fruit. Obviously, too, such machines were only adapted to hard, smooth fruits such as apples, and could not be used with softer fruits, berries, or vegetables.

Washing. Through the Bureau of Chemistry an acid solution was developed and patented in 1926. Soon thereafter several commercial machines appeared on the market, particularly in the Pacific Northwest, where the residue problem first became acute. Subsequently, due in some measure to the imposition of a lead tolerance, these machines have been developed and refined. At present, fruit washers are almost universally used in nearly all fruit growing regions. Washers have been devised in greatest numbers for apples, pears, and citrus fruits, but other edible products as well have been successfully washed.

The general principle of all fruit washers is similar: the fruits are exposed to a chemical bath which may be either acid or alkaline, or in the "tandem" washers one of each, followed by a rinsing with pure water. The mechanisms which have been devised to propel the fruits through the washing bath are varied, and rather

elaborate machines have appeared, some equipped with driers and heaters.

In addition to hand dipping of fruits, a procedure only useful for small lots of fruits, two types of fruit washers are available, flotation and the brush washers.

Flotation Washers. In this type of washer, a typical variety of which is shown in figure 20, the fruits are dumped into a rectangular

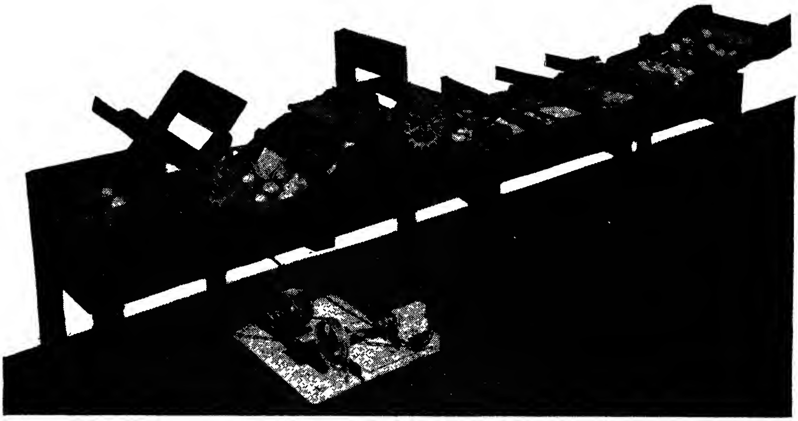

FIG. 20. Homemade flotation apple washer, capacity 1000 bushels per day. Designed by A. W. Clyde.

tank containing the wash solution and propelled through the bath by a suitable mechanical means, such as a conveyor belt or paddle wheels. The speed of the conveyor regulates the exposure. From the washing solution the fruits pass into a bath of running water and as a final precaution are rinsed with a pressure spray of clean water. Certain types of machines are equipped with driers to remove the excess moisture, but it appears that packing the apples in a wet condition does not affect the keeping qualities of the fruit.[7]

Flotation washers are of a number of types, most of them being modeled after the "Oregon washer" devised in 1927 by the workers at the Oregon Agricultural Experiment Station.[8] Such washers as this, the "Cornell washer," [9] and others are homemade; that is, their construction is relatively simple so that they may be assembled from commonly available materials by any one with a fair degree of mechanical ability at a cost of approximately one

hundred dollars. Commercial machines, more elaborate in construction, are also available.

Flotation washers, when properly used on fruit with a relatively low level of residue (3 to 4 times tolerance), work quite satisfactorily using cold hydrochloric acid solution. For heavier deposits, the wash solution may be heated, but in general the efficiency of removal accomplished by this type of machine is not so great as that from the mechanical brush type of washer.

Brush Washers. In this type of washer the fruits are subjected not only to the solvent action of the wash solution, but in addition to a mechanical scrubbing action usually accomplished by a series of revolving brushes. The combined action is obviously highly efficient and such machines are to be recommended where fruits contain excessively high deposits of spray residue. A number of different types of brush washers are available commercially. Due to their more complicated mechanism, they are more expensive than the flotation type washers.

CHEMISTRY OF SPRAY RESIDUE REMOVAL

Solubility of Spray Deposits. In discussing the removal of spray residues from the surfaces of fruits, a distinction should be made between true solubility, in which both lead and arsenic of lead arsenate for example go into solution in equimolecular ratio, and chemical reactions in which one of the elements may form a more soluble salt, and hence be removed in larger quantities than the other.

From a practical point of view, it makes no difference which factor operates, the main consideration being the removal of the spray deposit. The presence of two toxic elements in the molecule of lead arsenate, however, makes it imperative that both be removed in approximately the same ratio in which they are present in the parent compound. This, of course, holds true only when the legal limits for lead and arsenic are in approximately this ratio as well.

Robinson [10] and Carter [11] have studied a number of solvents for the removal of lead arsenate. Carter's results for certain common acids are given in Table 5.

From this table it may be seen that among the common inorganic acids hydrochloric acid was the most effective in dissolving

TABLE 5

SOLVENT ACTION OF ACIDS ON LEAD ARSENATES

Solvent	*Concentration*	Grams $PbHAsO_4$ per 100 cc.	
		From As determinations	From Pb determinations
Hydrochloric acid, 0.5%	0.1359 N	0.258	0.250
*Hydrofluosilicic acid	0.1359 N	0.050	0.066
Perchloric acid	0.1359 N	0.162	0.164
Nitric acid	0.1359 N	0.199	0.188
Sulfuric acid	0.1359 N	1.822	0.003
Sulfuric acid	0.0679 N	0.852	Not run
Chromic acid	0.1359 N	1.666	0.008
*Phosphoric acid	0.1359 N	0.030	0.009
Acetic acid	0.1359 N	0.002	0.002
Dichloracetic acid	0.1359 N	0.147	Not run
Trichloracetic acid	0.1359 N	0.163	0.147

* Hydrofluosilicic acid considered to yield six replaceable hydrogen atoms per mole and phosphoric acid two: data from Carter.[11]

both lead and arsenic. If one were concerned solely with arsenic removal, acids such as sulfuric or chromic would be highly satisfactory, but because of the formation of insoluble lead salts practically none of the latter element is removed. Carter further found that mixed acids or acids and salts did not materially increase the solvent action. Robinson [10] in the earlier paper and Carter [11] both found the solutions of salts tested to be of little value, although the use of common salt, sodium chloride, in addition to hydrochloric acid has been recommended by a number of workers.

Of the other materials tested as solvents, certain alkaline substances have been determined to be relatively efficient. Of these, sodium hydroxide was found by Carter to be the best, but apparently it caused fruit injury. Sodium silicate was also found to be a good solvent, removing nearly equal quantities of lead and arsenic.

Not much information is available on the solubility of toxic spray residues other than lead arsenate, although it has been determined that either dilute hydrochloric acid or sodium silicate are fairly satisfactory for the removal of cryolite spray residues.

In this connection, Carter [12] found that the addition of sodium chloride to hydrochloric acid reduced the solubility of cryolite, although certain other salts, such as boric acid, aluminum or ferric salts increased the solubility of cryolite in dilute hydrochloric acid.

Factors Complicating Residue Removal. The fact that stickers, such as casein compounds and oils, may increase the difficulty with which spray residues may be removed has been mentioned. Frear and Worthley [13, 14] found that when dried skimmilk powder was used in the spray mixture it appeared to facilitate removal of lead, but that fish oil produced a residue resistant to washing. Weber, McLean, Driggers, and O'Neill,[15] in a comprehensive study of a number of combinations of stickers and spreaders in lead arsenate sprays, found that the combinations with summer oil were the most difficult to wash. This finding agrees with all previous work, which has indicated that mineral oil sprays produce particularly tenacious deposits.

Resistant deposits produced by the use of mineral oils have been washed by Robinson [16] with hydrochloric acid to which has been added organic solvents such as alcohol, benzol, or kerosene and it appears to be a common procedure in the Northwest to use "tandem" washing, one bath of dilute acid with an oil such as kerosene, followed by a bath of sodium silicate (usually 60 pounds of commercial silicate—water glass—per 100 gallons of water). Such a combination is said to be highly effective, particularly when the bath temperatures are raised to 100°–110° F.[17]

In this connection Cohee and St. John [18] have pointed out that one of the components of the natural wax of the apple, ursolic acid, may form insoluble lead salts difficult to remove. This is borne out by the fact that from fruit bearing a heavy coating of wax it is usually more difficult to remove the lead than the arsenic.[13] Recently, McLean and Weber [19] have stated that insect residues, particularly the honeydew secreted by leaf hoppers, which is often covered with a fungus growth, caused difficulty in removal of lead residues from apples. These investigators also found that for a given spray treatment, the apples from trees with heavy foliage were easier to wash than those from trees with light foliage, possibly because of the excessive wax formation on the fruit from lightly foliated trees.

The use of wetting agents in the washing baths, first suggested by McLean and Weber [20] has apparently facilitated residue removal in some cases, particularly when heated washing baths are used. Some workers, however, have discovered no particular benefit from their use.[13, 21] It appears that the usefulness of these wetting agents is considerably lessened when the fruit to be washed is allowed to stand after picking for any period at room temperature. The most satisfactory types of wetting agents appear to be sulfonated aromatic derivatives. When used in washers having mechanical agitation or forced circulation of liquid, these wetting agents have a pronounced tendency to foam. This may be avoided by the use of an "anti-foam," usually a preparation containing wool-grease in some form.

The voluminous literature relating to spray residues and their removal has been collected and abstracted by Busbey.[22]

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Part V

Analytical Methods

CHAPTER XIV

MACRO ANALYTICAL METHODS

In the following pages are given methods for the chemical analysis of insecticides and fungicides. The list of methods is by no means complete; a number of highly satisfactory methods are omitted because of space limitations. In general, the methods given are those which have been used in the author's laboratory, or in laboratories with which he is familiar.

The methods presented are divided into two groups for convenience: the first, "Macro Methods," will deal with the analysis of fairly large quantities of materials, such as are available in studies of the gross composition of samples of commercial insecticides and fungicides. The second section, "Micro Methods," contains those methods particularly applicable to small quantities of material, such as those ordinarily present in spray residues on fruits, leaves, and the like. It is obvious that such a division is rather an arbitrary one.

Those methods marked either with an asterisk (*) or the letter (T) are respectively "official" and "tentative" methods reprinted from the *Official and Tentative Methods of Analysis* of the Association of Official Agricultural Chemists [1] with the kind permission of the editorial board. This valuable book should be in the hands of all analysts working in any branch of agricultural analysis.

Paris Green

***Moisture.**

Dry 2 g. to constant weight at 105°–110° C. and report loss of weight as moisture.

***Total Arsenic**—Hydrazine sulfate method.[2, 3]

Reagents

(*a*) *Hydrazine sulfate-sodium bromide solution.* Dissolve 20 g. $N_2H_4 \cdot H_2SO_4$ and 20 g. NaBr in 1 liter of 1 + 4HCl (1 part HCl to 4 parts water).

(*b*) *Standard bromate solution.* Dissolve 1.525 g. of $NaBrO_3$ in water and make to 1 liter.

(*c*) *Standard arsenious oxide solution.* Dissolve exactly 2 g. of pure As_2O_3 in a beaker by boiling with 150–200 ml. of water containing 10 ml. H_2SO_4; cool and transfer to a 500-ml. volumetric flask and make to mark. 1 ml. of this solution contains 4 mg. of As_2O_3.

(*d*) *Methyl orange indicator.* Dissolve 0.5 g. of methyl orange in water and dilute to 1 liter.

APPARATUS

Distillation flask of 500-ml. capacity supported on metal gauze over asbestos board with circular opening to direct flame only to bottom of flask. This flask is fitted with a dropping funnel and connected by a condenser with a 500-ml. receiving flask containing 40 ml. H_2O. Second receiving flask of same size contains 100 ml. H_2O (see figure 21). The receiving flasks are cooled by placing them in a pan of cold water.

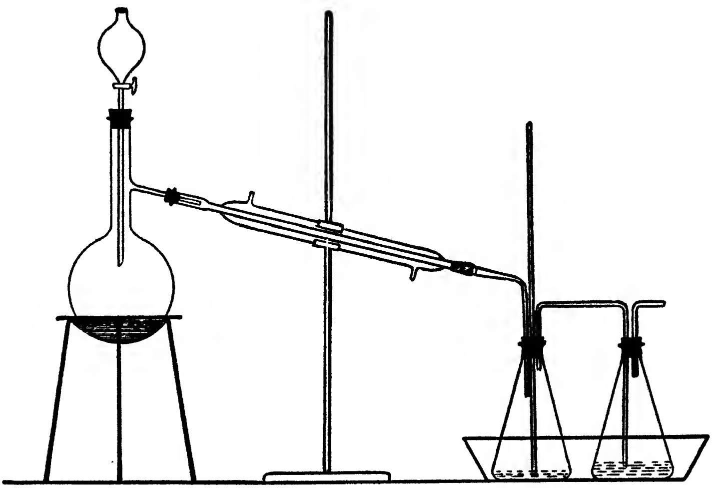

FIG. 21. Arsenic distillation apparatus.

Standardization.

Pipette 25 ml. aliquots of standard arsenic solution (*c*) into a 500-ml. Erlenmeyer flask, add 15 ml. HCl, dilute to 100 ml. and heat to 90° C. Titrate with sodium bromate solution (*b*), adding 10 drops of indicator (*d*) near the end of titration, and adding bromate solution slowly near the end of titration. Agitate thoroughly during titration.

Determination.

Weigh out a sample containing not more than 0.4 g. of As and transfer to distilling flask. Add 50 ml. of reagent (*a*), close flask and connect to condenser and receiving flasks. Boil 2–3 minutes, add 100 ml. HCl by means of the dropping funnel, and distill until volume in distilling flask is approximately 40 ml. Add 50 ml. HCl, and continue distillation until volume in flask is again approximately 40 ml. Disconnect flask, wash down condenser, and transfer contents of receiving flask to liter volumetric flask, make to volume, and mix thoroughly. Pipette a 200-ml. aliquot of the distillate into a 500-ml. Erlenmeyer flask, add 10 ml. HCl and titrate with standard bromate solution as described under "Standardization."

From the number of ml. of standard solution used, calculate the percentage of arsenic in sample.

***Total Arsenious Oxide.**[4]

(This method determines only the trivalent arsenic (As_2O_3). Antimony in the trivalent form and ferrous and cuprous salts vitiate the results.)

Weigh 1.5 g. of sample and wash into 250-ml. volumetric flask with 100 ml. of HCl (1 + 4), heating to a maximum of 90° C., if necessary, to secure complete solution of sample. Cool, and make to volume. Heat should be avoided, if possible.

Transfer 50-ml. aliquot to 500-ml. Erlenmeyer flask, add 10 ml. of HCl, heat to 90° C., and titrate with the standard bromate solution as directed under "Total arsenic."

From the number of ml. of bromate solution used calculate the percentage of As_2O_3.

***Water Soluble Arsenious Oxide.**

REAGENTS

(*a*) *Standard iodine solution.* Approximately 0.05 N. Mix 6.35 g. of pure iodine with twice this weight of pure KI, dissolve in a small quantity of water, filter, and dilute filtrate to 1 liter in volumetric flask. Standardize against standard arsenious oxide solution (see reagent (*c*), total arsenic, page 210) as follows: Pipette 50 ml. of the As_2O_3 solution into an Erlenmeyer flask, dilute to same volume as that of aliquot used for titration in actual

determination, neutralize with $NaHCO_3$, add 4–5 g. in excess, and add the standard iodine solution from a buret, shaking flask continuously until yellow color disappears slowly from the solution. Add 5 ml. of starch solution (*b*), and continue adding the iodine solution, dropwise, until a permanent blue color is obtained. Calculate the value of the standard iodine solution in terms of As_2O_3. For conversion of As_2O_3 to As_2O_5, multiply by 1.1617.

(*b*) *Starch indicator.* Mix approximately 2 g. of finely powdered potato starch with cold water to a thin paste; add approximately 200 ml. of boiling water, stirring constantly, and immediately discontinue heating. Add approximately 1 ml. of metallic mercury, shake, and allow starch to stand over the mercury.

Determination.

To 1 g. of sample in liter Florence flask add 1 liter of recently boiled water that has been cooled to 32° C. Stopper flask and place in water bath kept at 32° by means of thermostat. Digest for 24 hours, shaking hourly for 8 hours during this period. Filter through dry filter and transfer 250 ml. of filtrate to Erlenmeyer flask; add 4–5 g. of $NaHCO_3$ and titrate with standard iodine solution, using starch indicator. Correct for quantity of iodine solution to produce same color, using same reagents and volume. Calculate quantity of As_2O_3 present and express results as percentage of water-soluble As_2O_3.

***Total Copper Oxide.** *Electrolytic Method.*

Treat 2 g. of sample in beaker with 100 ml. of water and approximately 2 g. of NaOH and boil thoroughly until all copper is precipitated as Cu_2O. Filter, wash well with hot water, dissolve precipitate in hot HNO_3 $(1 + 4)$, cool, transfer to a 250-ml. volumetric flask and dilute to mark. Electrolyze aliquot of 50 or 100 ml., using either a weighed 150-ml. Pt dish as cathode and a rotating anode or a 150-ml. beaker with a weighed Pt gauze cathode. Use a current of approximately 3 amperes. After all the copper has been deposited (usually 30 minutes is sufficient) and while current is still flowing, wash deposit of copper with water by siphoning. Interrupt current, rinse cathode in alcohol, dry for a few minutes in oven, and weigh. Calculate percentage of copper in sample.

Volumetric Method.[5]

REAGENT

(*a*) *Standard thiosulfate solution.* Prepare a solution containing 39 g. of pure $Na_2S_2O_3 \cdot 5H_2O$ in 1 liter. Standardize against a copper solution of known concentration, following the titration procedure given below.

Determination.

Take a suitable aliquot of the HNO_3 solution of Cu_2O described above, treat with NH_4OH in excess, boil until excess NH_3 is expelled, as shown by change of color in liquid and partial precipitation. Add 3–4 ml. of 80 per cent acetic acid, boil 1–2 minutes, cool, add 10 ml. of a 30 per cent KI solution and titrate with standard thiosulfate solution (reagent *a*) until brown color becomes faint. Add starch indicator (reagent *b*, p. 212) and continue titration until blue color due to free iodine is entirely vanished. From the number of ml. of standard thiosulfate calculate the percentage of copper in the sample.

CALCIUM ARSENATE

***Moisture**—see Paris green.

***Total Arsenic**—see Paris green.

***Total Arsenious Oxide.**[6]

(*a*) *Not applicable in the presence of nitrates.* Weigh 1 g. of sample, transfer to 500-ml. Erlenmeyer flask, and dissolve in 100 ml. of HCl (1 + 3). Heat to 90° C. and titrate with standard bromate solution (see total arsenic in Paris green), using 10 drops of methyl orange indicator. From number of ml. of standard bromate solution used calculate percentage of As_2O_3

(*b*) *Applicable in presence of small quantities of nitrates.* Proceed as in (*a*), except make titration at room temperature.

***Water Soluble Arsenic.**

REAGENT

Sodium thiosulfate (approximately 0.05 N). Dissolve 31 g. of crystalline $Na_2S_2O_3 \cdot 5H_2O$ in water and make to a volume of 1 liter.

Determination.

In a liter Florence flask place a 2 g. sample (4 g. if a paste) of the material to be tested, 1 liter of recently boiled water that has been cooled to 32° C. Stopper flask and maintain at a constant temperature of 32° C. in a thermostatically controlled water bath for 24 hours, shaking hourly for 8 hours during this time. Filter through dry paper, using Buchner funnel and filter-aid if necessary, in which case the first 50 ml. of filtrate should be discarded. Transfer an aliquot of 250–500 ml. of clear filtrate to an Erlenmeyer flask, add 3 ml. of H_2SO_4 and evaporate on a hot plate to a volume of approximately 100 ml. At this point add 1 g. KI, and continue boiling until volume is approximately 40 ml. Cool, dilute to approximately 200 ml., and add $Na_2S_2O_3$ solution dropwise until the iodine color is exactly removed. Neutralize with $NaHCO_3$, add 4–5 g. in excess, titrate with standard iodine solution (*a*, p. 211) until yellow color disappears slowly, add 5 ml. of starch indicator (*b*, p. 212) and continue titration to a permanent blue color. Make blank determination, using all reagents, and make correction. Calculate the percentage of water soluble arsenic from corrected amount of standard iodine solution used.

Water Soluble Arsenic. "Geneva Method" of Pearce, Norton, and Chapman.[7]

A 0.5 g. sample is weighed into a 500-ml. Erlenmeyer flask and 100 ml. of water added. The suspension is allowed to stand with frequent shaking for 2 or 3 hours. Three drops of a 1 per cent alcoholic solution of thymolphthalein are added, and the mixture is titrated with a freshly prepared solution of carbon dioxide, approximately 0.02 N, until the blue color disappears permanently. In most cases, some blue color reappears on standing for a few minutes and several drops more of the carbon dioxide solution must be added. Samples have occasionally been found which require additions of the reagent over a period of several hours before a permanent end-point is reached. After the titration, enough water is added to bring the total volume up to 250 ml. and the sample is allowed to stand for 24 hours, with occasional shaking. The suspension is then filtered through a dry filter, and the arsenic determined in a convenient aliquot of the filtrate by the following method: Add 20 ml. H_2SO_4 and several ml. HNO_3

to a 100-ml. aliquot of the filtrate in an 800 ml. Kjeldahl flask. Evaporate to SO_3 fumes, cool, add 50 ml. of water, and again evaporate to SO_3 fumes. Cool, add 25 ml. of water, and cool again. Add 20 g. of NaCl and 25 ml. of a solution of 20 g. of hydrazine sulfate and 20 g. of NaBr per liter of HCl (1 + 4). Connect Kjeldahl flask to 300-ml. Erlenmeyer containing 100 ml. of water by means of a bent glass tubing extending under the surface of the water in the Erlenmeyer flask, as shown in figure 25, p. 255. Heat Kjeldahl flask at such a rate that the liquid in the receiving flask reaches a temperature of 90° C. in from 9 to 11 minutes. When liquid reaches 90° C. remove and titrate with standard bromate solution using methyl orange indicator (see total arsenic in Paris green, p. 210). Calculate percentage of water soluble arsenic as As_2O_3.

***Total Calcium Oxide.**[6]

REAGENTS

(*a*) *Ammonium oxalate solution.* Dissolve 40 g. of $(NH_4)_2$-$C_2O_4 \cdot H_2O$ in 1 liter of water.

(*b*) *Standard potassium permanganate solution.* Dissolve 3.161 g. of $KMnO_4$ in freshly distilled water and dilute to 1 liter. Filter through asbestos in Gooch crucible and allow to stand several days in dark place. To standardize, dissolve 0.25 g. of pure $Na_2C_2O_4$ in water, add 25 ml. of H_2SO_4 (1 + 4), dilute to 200 ml., heat to approximately 70° C. and titrate with the $KMnO_4$ solution until the solution assumes a faint pink color. From this titration calculate the concentration of $KMnO_4$ solution, which should be about 0.1 N.

Determination.

Dissolve 2 g. of sample in 80 ml. of acetic acid (1 + 3), transfer to 200-ml. volumetric flask, dilute to volume, and filter through a dry filter. Transfer 50-ml. aliquot to beaker, dilute to approximately 200 ml., heat to boiling and precipitate the calcium with the ammonium oxalate solution (reagent *a*). Allow beaker to stand 3 hours on steam bath, filter, and wash precipitate with hot water. Dissolve precipitate in 200 ml. of water containing 25 ml. of H_2SO_4 (1 + 4), heat to 70° C. and titrate with the $KMnO_4$ solution. From the number of ml. of $KMnO_4$ solution used calculate percentage of CaO.

LEAD ARSENATE

***Moisture.**

(*a*) *Powder.* Dry 2 g. to constant weight at 105°–110° C. and report loss in weight as moisture.

(*b*) *Paste.* Proceed as directed under (*a*), using 50 g. Grind dry sample to fine powder, mix well, transfer small portion to sample bottle and again dry for 1–2 hours at 105°–110° C. Use this anhydrous material for determination of total PbO and total arsenic.

***Total Arsenic**—see Paris green.

***Total Arsenious Oxide.**[8]

Weigh 2 g. of powdered sample and transfer to 200-ml. volumetric flask, add 100 ml. of H_2SO_4 (1 + 6) and boil 30 minutes. Cool, dilute to volume, shake thoroughly, and filter through dry filter. Nearly neutralize 100 ml. of filtrate with NaOH solution (40 per cent), using a few drops of phenolphthalein indicator. If neutral point is passed, make acid again with the dilute H_2SO_4. Neutralize with $NaHCO_3$, add 4–5 g. in excess and titrate with approximately 0.05 N standard iodine solution (*a*, p. 211), using starch indicator near the end. Calculate the percentage of As_2O_3 from the number of ml. of standard iodine used.

Total Arsenic Oxide.[8] (T)

REAGENTS

(*a*) *Potassium iodide solution.* Dissolve 20 g. of KI in water and dilute to 100 ml.

(*b*) *Ammonium chloride solution.* Dissolve 250 g. of NH_4Cl in water and dilute to 1 liter.

(*c*) *Standard thiosulfate solution* (approximately 0.05 N). Dissolve 13 g. of $Na_2S_2O_3 \cdot 5H_2O$ in recently boiled and cooled water and dilute to 1 liter with recently boiled and cooled water. Standardize as follows:

Prepare pure $PbHAsO_4$ by pouring a solution of $Pb(NO_3)_2$ into a solution of KH_2AsO_4, which should be in excess. Collect precipitate by filtration, dissolve it in the smallest possible quantity of boiling HNO_3 (1 + 4) and pour this solution into a large volume of water (50–100 ml. of HNO_3 solution into 2–3 liters of water). Collect precipitate by filtration and dry at 110° C.

Dissolve a weighed quantity (approximately 0.7 g.) of the pure $PbHAsO_4$ prepared as above, in 50 ml. of HCl in Erlenmeyer flask. If necessary to effect solution, heat on steam bath, keeping flask covered with watch glass to prevent evaporation of acid. Cool to 20°–25° C., add 10 ml. of KI solution (reagent *a*) and 50 ml. (or more if necessary to produce a clear solution) of NH_4Cl solution (reagent *b*), and immediately titrate liberated iodine with the standard thiosulfate. When color becomes faint yellow, dilute with approximately 150 ml. of water and continue titration carefully, dropwise, until colorless, using starch indicator (*b*, p. 212) near end point. From weight of $PbHAsO_4$ and the number of ml. of $Na_2S_2O_3$ solution used calculate the value of the latter in terms of As_2O_5

Determination.

Weigh 0.5 g. of powdered sample and transfer to an Erlenmeyer flask. Add 25–30 ml. of HCl and evaporate to dryness on steam bath. Add 50 ml. of HCl and proceed as directed above under standardization, beginning with "If necessary to effect solution, heat on steam bath." From the number of ml. of standard thiosulfate solution used calculate the percentage of As_2O_5.

***Water Soluble Arsenic**—see Calcium arsenate.

***Lead Oxide.**[9, 10]

Weigh 1 g. of powdered sample and transfer to a beaker. Add 5 ml. HBr (approximately 1.38 specific gravity), 15 ml. HCl and evaporate to dryness. Add 5 ml. HBr and 20 ml. HCl and again evaporate to dryness. Add 25 ml. 2 N HCl, heat to boiling and filter immediately to remove silica. Wash filter with boiling water until filtrate has a volume of 125 ml. See that all lead is in solution before filtering, adding 25 ml. additional to 2 N HCl and washing to a volume of 250 ml. if necessary. Pass in H_2S until precipitation is complete, filter and wash precipitate thoroughly with 0.5 N HCl saturated with H_2S. Zinc may be determined in filtrate and washings. Transfer filter paper containing the sulfides of Pb and Cu to a 400-ml. Pyrex beaker and completely oxidize all organic matter by heating on steam bath with 4 ml. of H_2SO_4 and about 20 ml. of fuming HNO_3 in a covered beaker. Evaporate on steam bath and then completely remove HNO_3 by heating on

hot plate until copious fumes of H_2SO_4 appear. Cool, add a few ml. of water and again heat to fuming to remove last traces of HNO_3. Cool, add 50 ml. H_2O and 100 ml. alcohol, allow to stand several hours or overnight. Filter, through a weighed Gooch crucible previously washed with water, acidified alcohol (100 parts water, 200 parts alcohol and 3 parts H_2SO_4), alcohol, and finally dried at 200° C. Wash the precipitate of $PbSO_4$ into this crucible, washing about 10 times with acidified alcohol, and then with alcohol to remove the H_2SO_4 (copper may be determined in this filtrate if the original material contained Bordeaux mixture in combination with an arsenate). Dry at 200° C. to constant weight, keeping crucible covered to avoid loss from spattering. From weight of $PbSO_4$ calculate percentage PbO in sample, using factor 0.7360.

***Copper** (in Bordeaux-lead arsenate mixtures, etc.) *Electrolytic Method.*[6]

Evaporate filtrate and washings from the $PbSO_4$ precipitate (in previous method) to fuming; add a few ml. of fuming HNO_3 to destroy organic matter, and again evaporate until fumes of H_2SO_4 appear. Take up with approximately 100 ml. of water, add 1 ml. HNO_3 and filter if necessary. Electrolyze, following the procedure described under Paris green. The volumetric method for copper described under Paris green may also be used on mixtures of this kind.

MAGNESIUM ARSENATE

***Moisture**—see Paris green.
***Total Arsenic**—see Paris green.
***Total Arsenious Oxide**—see Lead arsenate.
***Water Soluble Arsenic**—see Calcium arsenate.

ZINC ARSENITE

***Moisture**—see Paris green.
***Total Arsenic**—see Paris green.
***Total Arsenious Oxide.**[4, 6]

Weigh 2 g. of sample and transfer to a beaker. Dissolve in 80 ml. of HCl (1 + 4) and wash into a 200-ml. volumetric flask and dilute to volume. Thoroughly mix solution and filter through

a dry filter. Transfer a 25 ml. aliquot to a 500-ml. Erlenmeyer flask, add 20 ml. of HCl and dilute to 100 ml. Heat to 90° C. and titrate with standard bromate solution (see total arsenic in Paris green), using 10 drops of methyl orange indicator.

***Water Soluble Arsenic**—see Calcium arsenate.

***Total Zinc Oxide.**[4, 6]

REAGENT

Mercury-thiocyanate solution. Dissolve 27 g. of $HgCl_2$ and 30 g. of NH_4SCN in water and dilute to 1 liter.

Determination.

Transfer a 25-ml. aliquot of the solution prepared for the determination of total arsenious oxide (see above) to a beaker and add 5 ml. of HCl. If there is much iron present, reduce it by adding a little $NaHSO_3$ and heating on steam bath until the odor of SO_2 has practically disappeared. Cool, dilute to approximately 100 ml., and add 35–40 ml. of Hg-thiocyanate reagent with vigorous stirring. Allow to stand at least one hour with occasional stirring. Filter through a weighed Gooch crucible, and wash with water containing 20 ml. of the Hg-thiocyanate reagent per liter, and dry to constant weight at 105° C. From this weight calculate percentage of ZnO, using factor 0.16332.

FLUORINE COMPOUNDS

Total Fluorine. **Lead Chlorofluoride Method.*[11]

REAGENTS

(*a*) *Fusion mixture.* Mix anhydrous Na_2CO_3 and K_2CO_3 in equimolecular proportions.

(*b*) *Lead chlorofluoride wash solution.* Dissolve 10 g. of $Pb(NO_3)_2$ in 200 ml. of H_2O; dissolve 1 g. of NaF in 100 ml. of H_2O and add 2 ml. of HCl; mix these 2 solutions. Allow precipitate to settle and decant supernatant liquid. Wash 4 or 5 times with 200 ml. of H_2O by decantation, and then add approximately 1 liter of cold H_2O to the precipitate and allow to stand 1 hour or longer, with occasional stirring. Pour through filter and use clear filtrate. By adding more H_2O to the precipitate of PbClF and stirring, more wash solution may be prepared as needed.

(c) *Standard silver nitrate solution.* 0.2 N. Standardize by titration against pure NaCl, using K_2CrO_4 indicator.

(d) *Standard potassium or ammonium thiocyanate solution.* 0.1 N. Standardize by comparing with the standard solution of $AgNO_3$ under the same conditions as obtain in the determination.

(e) *Ferric indicator.* Add to cold saturated solution of ferric alum (free from Cl) sufficient colorless HNO_3 to bleach the brown color.

(f) *Bromphenol blue indicator.* Grind 0.1 g. of the powder with 1.5 ml. of 0.1 N NaOH solution and dilute to 25 ml.

Determination.

Mix 0.5 g. (or less if necessary to make content of F fall between 0.01 and 0.1 g.) of sample with 6 g. of fusion mixture and 0.2–0.3 g. of powdered silica and heat to fusion over Bunsen burner. (Use of blast lamp is not required as it is only necessary that the mass be fluid, and it is preferable not to heat much beyond temperature at which it melts. If much Al is present, a uniform, clear, liquid melt cannot be obtained. There will be particles of a white solid separated in the liquid. The melt after cooling should be colorless, or at least should not have more than a gray color.) Leach cooled melt with hot H_2O, and filter when disintegration is complete. Return the insoluble residue to a Pt dish by the use of jet of H_2O, add 1 g. of Na_2CO_3, make the volume 30–50 ml., boil a few minutes, disintegrating any lumps with glass rod flattened on end, filter through same paper, wash thoroughly with hot H_2O, and adjust volume of filtrate and washings to approximately 200 ml. Add 1 g. of ZnO dissolved in 20 ml. of HNO_3 (1 + 9), boil 2 minutes with constant stirring, filter, and wash thoroughly with hot H_2O. Return the gelatinous mass to the beaker once or twice and thoroughly disintegrate in the wash solution because it is difficult to wash this precipitate on filter. (The mass can easily be returned to beaker by rotating funnel above beaker and at the same time cutting precipitate loose from paper with jet of wash solution.)

Add 2 drops of bromophenol blue and then the HNO_3 nearly to neutrality, leaving solution slightly alkaline. Boil solution gently with cover-glasses on the beakers, to expel CO_2. Finally add HNO_3 (1 + 4) until color just changes to yellow. Remove

from burners, add dilute NaOH until the color just changes to blue, and add 3 ml. of 10 per cent NaCl solution. Volume of solution at this point should be 250 ml.

Add 2 ml. of HCl (1 + 1) and 5 g. of $Pb(NO_3)_2$, and heat on steam bath. As soon as the $Pb(NO_3)_2$ is in solution, add 5 g. of Na acetate, stir vigorously, and digest on steam bath 30 minutes with occasional stirring. Allow to stand overnight at room temperature (4 hours will be sufficient unless much B is present). Decant solution through a paper of close texture; wash precipitate, beaker, and paper once with cold H_2O, then 4 or 5 times with a cool saturated solution of PbClF and then once more with cold H_2O.

Transfer precipitate and paper to beaker in which precipitation was made, stir paper to a pulp, add 100 ml. of HNO_3 (5 + 95), and heat on steam bath until precipitate is dissolved. (Five minutes is ample to dissolve this precipitate. If sample contains an appreciable quantity of sulfates the precipitate will contain $PbSO_4$, which will not dissolve. In such a case heat 5–10 minutes with stirring and consider the PbClF to be dissolved.) Add a slight excess of 0.2 N $AgNO_3$ solution, digest on steam bath 30 minutes, cool to room temperature while protected from light, filter, wash with cold H_2O, and determine $AgNO_3$ in the filtrate by titration with the standard thiocyanate solution, using 5 ml. of the ferric indicator. Subtract quantity of $AgNO_3$ found in the filtrate from that originally added. The difference will be that required to combine with the Cl in the PbClF, and from this difference calculate percentage of F in sample on basis that 1 ml. of 0.2 N $AgNO_3$ = 0.0038 g. of F.

NOTE: This method gives accurate results for quantities of F between 0.01 and 0.10 g. Below 0.01 g. the results have a tendency to be slightly low and above 0.1 slightly high. Satisfactory results are obtained in the presence of B and Al. This method should be used for all samples of fluorides that contain kaolin or fuller's earth as a filler.

If sample contains appreciable quantity of S, the S should be removed with CS_2 and F determined on air-dry residue, allowance being made in calculations for percentage of S removed.

With water-soluble samples, in absence of organic matter or other interfering substances, fusion may be omitted and determi-

nation made on aliquot of a water-soluble solution as directed above, beginning "Add 2 drops of bromophenol blue."

TOBACCO AND NICOTINE PREPARATIONS

Nicotine. **Silicotungstic Acid Method.*[12]

REAGENT

Silicotungstic acid solution. Dissolve 120 g. of silicotungstic acid ($4H_2O \cdot SiO_2 \cdot 12WO_3 \cdot 22H_2O$) in H_2O and dilute to 1 liter. (This acid should be white or pale yellow crystals, free from green color. The solution should be free from cloudiness and green color. Of the several silicotungstic acids, $4H_2O \cdot SiO_2 \cdot 10WO_3 \cdot 3H_2O$ and $4H_2O \cdot SiO_2 \cdot 12WO_3 \cdot 20H_2O$ do not give crystalline precipitates with nicotine and should not be used.)

Determination.

Weigh a quantity of the preparations that will contain preferably 0.1–1.0 g. of nicotine. If sample contains very little nicotine (about 0.1 per cent) do not increase quantity to point where it interferes with distillation. Wash with H_2O into 500-ml. Kjeldahl flask; and, if necessary, add a little paraffin to prevent frothing and a few small pieces of pumice to prevent bumping. Add a slight excess of NaOH solution, using phenolphthalein indicator, and close flask with rubber stopper through which passes stem of trap bulb and inlet tube for steam. Connect by means of trap bulb to well-cooled condenser, the lower end of which dips below surface of 10 ml. of HCl (1 + 4) in suitable receiving flask. Distil rapidly with current of steam. When distillation is well under way heat distillation flasks to reduce volume of liquid as far as practicable without bumping or undue separation of insoluble matter. Distil until a few ml. of distillate shows no cloud or opalescence when treated with drop of the silicotungstic acid and drop of HCl (1 + 4). Confirm alkalinity of residue in distillation flask with phenolphthalein indicator. Make distillate, which may amount to 1000–1500 ml. to convenient volume (solution may be concentrated on steam bath without loss of nicotine); mix well, and pass through dry filter if not clear. Test distillate with methyl orange to confirm its acidity. Pipette aliquot containing about 0.1 g. of nicotine into beaker (if samples contain very small quantities of nicotine, an aliquot containing as little as 0.01 g. of nicotine may be

used); add to each 100 ml. of liquid 3 ml. of HCl (1 + 4), and 1 ml. of silicotungstic acid for each 0.01 g. of nicotine supposed to be present. Stir thoroughly and let stand overnight at room temperature. Before filtering, stir precipitate to see that it settles quickly and is in crystalline form, filter on an ashless filter, and wash with HCl (1 + 1000) at room temperature. Continue washing for 2 or 3 fillings of filter after no more opalescence appears when a few ml. of fresh filtrate are tested with a few drops of nicotine distillate. Transfer paper and precipitate to a weighed Pt crucible, dry carefully, and ignite until all C is destroyed. Finally heat over Meker burner for not more than 10 minutes. Weight of residue $\times$ 0.1140 = weight of nicotine present in aliquot.

Silicotungstic Acid Method of Avens and Pearce.[13]

APPARATUS

The apparatus consists of a 500-ml. Pyrex Florence flask, *A*, used to generate steam, which is passed through the delivery tube, *B*, under the surface of the liquid in distilling flask, *C*. The steam generator has a three-hole rubber stopper. One hole carries the steam outlet tube, another a glass stopcock which serves to relieve excess pressure, and through the third passes about 90 cm. (3 ft.) of 6-mm. tubing for a pressure gage.

The 50-ml., round-bottomed, Pyrex distilling flask, *C*, is connected through a two-hole rubber stopper and by means of a safety trap, *D*, with a small vertical water condenser, *E*. The delivery tube, *F*, is adjusted in such a way that it dips beneath the surface of the liquid in the 200-ml. Pyrex beaker, used to receive the distillate. Rubber connections are used as shown in Fig. 22. Changes in steam pressure can be obtained by adjusting the stopcock opening or by controlling the flame of the Bunsen burner. A small microburner is used to keep the liquid in the distilling flask as low as desired. The entire outfit is assembled on a single ring stand. It can be moved around as desired and does not occupy more than 0.6 sq. meters (2 ft. square) of horizontal space.

PROCEDURE

It is desirable to use for analysis a sample that contains from 5 to 10 mg. of nicotine, but as little as 2 mg. or less can be determined by this method. Tobacco dusts and other dry preparations

of nicotine are usually weighed directly into the distilling flask. In the case of liquid preparations, such as nicotine sulfate solutions of high nicotine content, it is more convenient to weigh the sample in a weighing bottle, transfer it to a suitable volumetric flask, dilute to volume, and pipet a 5-ml. aliquot into the distilling flask. The sample is covered with 2 to 3 ml. of water, and 2 drops of phenolphthalein indicator solution are then added. Sodium hydroxide solution (about 40 per cent) is introduced in slight excess as determined by the indicator. The flask is immediately attached to

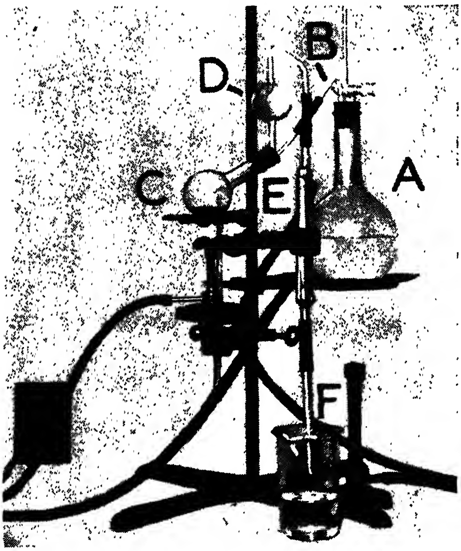

FIG. 22. Apparatus for the distillation of nicotine, method of Avens and Pearce.

the outfit and steam is passed into it. A steam pressure of 1.5 to 2 feet (45.7 to 60.9 cm.) of water is maintained throughout the run. The beaker used to receive the distillate contains 3 ml. of hydrochloric acid (1 to 4) and about 5 ml. of water. As soon as the distillation proceeds at a smooth rate, the microburner should be used to reduce the volume of liquid in the flask. Distillation is continued for 30 minutes, at the end of which time the liquid in the distilling flask should be reduced almost to dryness and the volume of distillate should preferably not exceed 100 ml. When the dis-

tillation is complete the condenser and delivery tube are washed out and the volume of distillate is adjusted to about 100 ml.

To precipitate the nicotine, 1 ml. of silicotungstic acid (12 per cent solution) is used for every 10 mg. of nicotine or less. After precipitation, the covered samples are heated on the steam bath for 15 minutes, cooled slowly to room temperature, and maintained at 0° to 10° C. overnight. The samples are filtered through C. S. and S., No. 589, white ribbon filter paper, and washed with 100 to 200 ml. of hydrochloric acid (1 to 2000). Transfer paper and precipitate to a weighed platinum crucible, dry carefully, and ignite until all carbon is destroyed. Finally heat over a Meker burner for not more than 10 min. Weight of residue $\times$ 0.1140 = weight of nicotine present in aliquot.

PYRETHRUM PREPARATIONS [14]

PYRETHRUM POWDER

Pyrethrin I. **Mercury Reduction Method.*

REAGENTS

(*a*) *Denigès reagent.* Mix 5 g. of yellow HgO with 40 ml. of H_2O and, while stirring, slowly add 20 ml. of H_2SO_4; then add another 40 ml. portion of H_2O and stir until completely dissolved. Test for absence of mercurous Hg by adding a few drops of (*b*) to 10 ml. and titrating with (*c*) as directed under "Determination," beginning "Add 30 ml. of HCl."

(*b*) *Iodine monochloride solution.* Dissolve 10 g. of KI and 6.44 g. of KIO_3 in 75 ml. of H_2O; add 75 ml. of HCl and 5 ml. of $CHCl_3$ in glass-stoppered bottle and adjust to faint I color (in $CHCl_3$) by adding dilute KI or KIO_3 solution. If there is much I set free, use a stronger solution of KIO_3 than 0.01 M at first, making final adjustment with 0.01 M solution. Keep in dark cupboard and readjust when necessary.

(*c*) *Standard potassium iodate solution.* 0.01 M. Dissolve 2.14 g. of pure KIO_3, previously dried at 105° C., in H_2O and dilute to 1 liter. 1 ml. of this solution = 0.0044 g. of Pyrethrin I, and needs no further standardization.

Determination.

Extract a quantity of sample that will contain 20–75 mg. of Pyrethrin I (12.5–20 g.) in Soxhlet or other efficient extraction

apparatus 7 hours with petroleum benzin, and evaporate petroleum benzin on water bath, heating no longer than necessary to remove solvent. Do not pass a current of air through flask during evaporation.

Add 15–20 ml. of 0.5 N alcoholic NaOH solution to the flask containing pyrethrum extract, connect to a reflux condenser and boil gently 1–1.5 hours. Transfer to a 600-ml. beaker and add sufficient H_2O to bring the volume to 200 ml. Add a few glass beads or preferably use boiling tube, and boil down to 150 ml. Transfer to a 250-ml. volumetric flask, add 1 g. of filter-cel and 10 ml. of 10 per cent $BaCl_2$ solution. Do not shake before making to volume. Make to volume, mix thoroughly, filter off 200 ml., neutralize with H_2SO_4 (1 + 4), and add 1 ml. in excess, using 1 drop of phenolphthalein as indicator. (If necessary to have the solution stand overnight at this point, it should be left in alkaline condition.) Filter through a 7 cm. filter paper that has been coated lightly with suspension of filter-cel in H_2O, on a Buchner funnel, and wash several times with H_2O. Transfer into a 500-ml. separatory funnel and extract with two 50-ml. portions of petroleum benzin. Wash extracts with 2 or 3 10-ml. portions of H_2O, and filter petroleum benzin extract through plug of cotton into clean 250-ml. separatory funnel. Wash cotton with 5 ml. of petroleum benzin. Extract petroleum benzin with 5 ml. of 0.1 N NaOH, shaking vigorously. Draw off the aqueous layer into 100-ml. beaker, wash the petroleum benzin with 5 ml. of H_2O or with an additional 5 ml. of 0.1 N NaOH, and add this to the beaker. Add 10 ml. of Denigès' reagent to the beaker and let stand 1 hour. Add 20 ml. of alcohol to beaker and precipitate the HgCl with 3 ml. of saturated NaCl solution. Warm to 60°, and filter through a small filter paper, transferring all precipitate to filter paper, and wash with 10 ml. or more of hot alcohol. Wash with two or more 10-ml. portions of hot $CHCl_3$, and place filter paper and contents in 250-ml. glass-stoppered Erlenmeyer flask. Add 30 ml. of HCl and 20 ml. of H_2O to the flask and cool; add 6 ml. of $CHCl_3$ or CCl_4 and 1 ml. of ICl solution and titrate with the iodate solution, shaking vigorously after each addition, until there is no iodine color in $CHCl_3$ layer. From the number of ml. of the standard iodate solution used in titration calculate percentage of Pyrethrin I in sample.

KIO_3 reacts with mercurous Hg to form mercuric Hg and I. Further addition of iodate in presence of HCl oxidizes I to ICl.

$$2Hg_2Cl_2 + KIO_3 + 6HCl \rightarrow 4HgCl_2 + ICl + KCl + 3H_2O$$

Addition of ICl does not change volume relationship between mercurous Hg and iodate solution and aids in determining end point in titration of small quantities of Hg. The endpoint is taken when red color disappears from $CHCl_3$ layer. The end point is not permanent; therefore titration should be completed rapidly with vigorous shaking after each addition of iodate.

***Pyrethrin II.**

Filter, if necessary, aqueous residue from petroleum benzin extraction in previous determination through Gooch crucible. Concentrate filtrate to about 50 ml., transfer to separatory funnel, and neutralize with $NaHCO_3$. Extract twice with $CHCl_3$ and wash $CHCl_3$ extract through 15 ml. of H_2O in each of two separatory funnels. Combine aqueous solution and washings, acidify strongly with HCl (approximately 8 ml.), saturate with NaCl, adding cautiously at first to prevent excessive ebullition of CO_2, and extract with 50 ml. of ethyl ether. Draw off aqueous layer into a second separatory funnel and extract again with 50 ml. of ether. Continue this extraction and drawing off of aqueous layer, using 35 ml. for third and fourth extractions. Wash the four ether extracts successively with 10 ml. of H_2O, and repeat with second successive washing with another 10 ml. of H_2O. Combine ether solutions, draw off any H_2O that separates, and filter through plug of cotton into 500-ml. Erlenmeyer flask. Evaporate ether on water bath and dry residue at 100° C. for 10 minutes. Add 2 ml. of neutral alcohol and 20 ml. of H_2O and heat to dissolve acid. Cool, filter through Gooch crucible, add drop or two of phenolphthalein indicator solution, and titrate with 0.02 N NaOH solution, of which 1 ml. = 0.00374 g. of Pyrethrin II.

PYRETHRUM EXTRACTS IN MINERAL OIL

Pyrethrin I. *Mercury Reduction Method.* (T)

REAGENTS—see under Pyrethrum powder.

Determination.

Weigh or measure a quantity of sample that will contain 20–75 mg. of Pyrethrin I, and transfer into 300-ml. Erlenmeyer flask.

Add 20 ml. or more if necessary of normal alcoholic NaOH solution to flask containing pyrethrum extract, connect to reflux condenser, and boil gently 1–1.5 hours. Transfer to 600-ml. beaker and add sufficient H_2O to make aqueous layer to 200 ml. If more than 20 ml. of alcoholic soda has been used, add sufficient H_2O so that all alcohol will be removed when volume has been reduced to 150 ml. Add a few glass beads, or preferably use boiling tube, and boil aqueous layer down to 150 ml. Transfer contents of beaker to 500-ml. separatory funnel and draw off aqueous layer into 250-ml. volumetric flask. Wash oil layer once with H_2O and add wash H_2O to aqueous portion. After drawing off aqueous layer and washings, if slight emulsion still persists, it may be broken by addition of 2–3 ml. of 10 per cent $BaCl_2$ solution. Do not shake vigorously after adding the $BaCl_2$; otherwise reversed emulsion that is difficult to separate may be formed. To aqueous solution in the 250-ml. flask, add 1 g. of filter-cel and 10 ml. or more of the $BaCl_2$ solution. Do not shake before making to volume. Make to volume, mix thoroughly and filter off 200 ml. Test filtrate with $BaCl_2$ to see if sufficient has been added to obtain clear solution. Neutralize with H_2SO_4 (1 + 4) and add 1 ml. in excess, using 1 drop of phenolphthalein as indicator. From this point, proceed as directed under pyrethrum powder, beginning "Filter through 7 cm. filter paper."

NOTE: Chrysanthemum monocarboxylic acid reacts with Denigès' reagent to form a series of colors beginning with phenolphthalein red, which gradually changes to purple, then blue, and finally to bluish green. The color reaction is very distinct with 5 mg. of monocarboxylic acid and quantities as low as 1 mg. can usually be detected. Therefore no Pyrethrin I should be reported if color reaction is negative.

When analyzing samples containing much perfume or other saponifiable ingredients such as thiocyanates, it may be necessary to use as much as 50 ml. of normal alcoholic NaOH.

DERRIS AND CUBE PREPARATIONS

Rotenone.[15] **Crystallization Method.*

Weigh 30 g. (if sample contains more than 7 per cent rotenone use a quantity that will give 1.0–1.5 g. of rotenone in the 200-ml. aliquot) of finely powdered root and 10 g. of decolorizing carbon into 500-ml. glass-stoppered Erlenmeyer flask. Add 300 ml. of $CHCl_3$ measured at definite room temperature; place flask on shaking machine and fasten stopper securely. Agitate vigorously for not less than 4 hours, preferably interrupting shaking with overnight rest (or flask may be shaken continuously overnight). Remove flask from machine and allow to cool in refrigerator for at least an hour. Filter mixture rapidly into suitable flask, using fluted paper without suction and keeping funnel covered with watch-glass to avoid loss from evaporation. Stopper flask and adjust temperature of filtrate to that of original $CHCl_3$.

Transfer exactly 200 ml. of this solution to 500-ml. Pyrex Erlenmeyer flask and distil until only about 25 ml. remains in flask. Transfer extract to 125-ml. Erlenmeyer flask, using CCl_4 to rinse out the 500-ml. flask. Evaporate almost to dryness on steam bath in current of air. Then remove remainder of solvent under reduced pressure, heating cautiously on steam bath when necessary to hasten evaporation (suction may be applied directly to flask). Dissolve extract in 15 ml. of hot CCl_4 and again, in similar manner, remove all solvent. Repeat with another 10–15 ml. portion of hot CCl_4. (This treatment removes all $CHCl_3$ from the resins. The $CHCl_3$ extract is usually completely soluble in CCl_4. If small quantities of insoluble material are present, the purification procedure described later will eliminate them. However, if large quantity of insoluble residue should remain when extract is dissolved in first portion of CCl_4, it should be filtered off and thoroughly washed with further portions of hot solvent, after which the filtered solution plus washings should be treated as directed above for removal of $CHCl_3$.)

Add exactly 25 ml. of CCl_4 and heat gently completely to dissolve extract. Cool flask in ice bath several minutes and seed with a few crystals of rotenone-CCl_4 solvate if necessary. Stopper flask and swirl until crystallization is apparent. If at this stage only a small quantity of crystalline material separates, add an

accurately weighed quantity of pure rotenone estimated to be sufficient to assure that final result, expressed as pure rotenone, is at least 1 g. Then warm to effect complete solution, and again induce crystallization. At the same time prepare saturated solution of rotenone in CCl_4 for washing. Place flasks containing extract and washing solution in ice bath capable of maintaining temperature of 0° and allow to remain overnight.

After 17–18 hours in ice bath, rapidly filter extract through weighed Gooch crucible fitted with disk of filter paper, removing flask from ice bath only long enough to pour each fraction of extract into crucible. Rinse residue of crystalline material from flask and wash under suction with sufficient of the ice-cold saturated solution (usually 10–12 ml.) to remove excess mother liquor. Allow crucible to remain under suction 5 minutes and then dry to constant weight at 40° C. (requires approximately an hour). The weight obtained is "crude rotenone-CCl_4 solvate."

Break up contents of crucible with spatula, mix thoroughly, and weigh 1 g. into 50-ml. Erlenmeyer flask. Add 10 ml. of alcohol that has previously been saturated with rotenone at room temperature, swirl flask a few minutes, stopper tightly, and set aside at least 4 hours, preferably overnight, at the same temperature. Filter on weighed Gooch crucible fitted with disk of filter paper. Rinse crystals from flask and wash under suction with solution of ethyl alcohol saturated with rotenone at temperature of recrystallization (10 ml. will usually be required). Allow crucible to remain under suction 3–5 minutes and then dry at 105° C. to constant weight, which should be effected in 1 hour.

Multiply weight, expressed in grams, by weight of crude rotenone-CCl_4 solvate, and to product add 0.07 g., which represents correction for rotenone held in solution in the 25 ml. of CCl_4 used in crystallization. If any pure rotenone has been added, subtract its weight from value obtained. This gives weight of pure rotenone contained in aliquot of extract, representing 20 g. of sample.

Alternative Extraction Procedure.

If sample is one in which ratio of rotenone to total extract is greater than 40 per cent, use quantity sufficient to contain 1.0–1.5 g. of rotenone and successively extract four times with $CHCl_3$,

using 200 ml. each for the second to fourth extractions. Filter after each extraction and return marc to flask for extraction with fresh solvent. Finally combine extracts, evaporate almost to dryness, and proceed as directed above, beginning at point where aliquot has been evaporated almost to dryness.

***Total Ether Extract.**

Extract 5 g. of finely powdered root in a Soxhlet or other efficient extraction apparatus with ethyl ether for 48 hours. After extraction, concentrate extract and filter off any insoluble material that may be present. Receive filtrate in tared beaker. Evaporate off ether on steam bath, and dry in oven at 105° C. to constant weight.

LIME SULFUR

***Total Sulfur.**[8] *Preparation of Sample.*

Weigh about 10 g. of solution, transfer to 250-ml. volumetric flask, and immediately dilute to mark with recently boiled and cooled H_2O. Mix thoroughly and transfer to number of small bottles, filling them completely and avoiding contact of solution with air as much as possible. Stopper bottles, seal with paraffin, and preserve in dark, cool place.

Determination.

Dissolve 2–3 g. of Na_2O_2 in 50 ml. of cold H_2O in 250-ml. beaker. Transfer 10-ml. aliquot of the prepared solution to this aqueous solution of Na_2O_2, keeping tip of pipette constantly just under surface of liquid until necessary to raise it for drainage at end. Use clean dry pipette for measuring each portion. Cover beaker with watch-glass and heat on steam bath, with occasional stirring, until all S is oxidized to sulfate (indicated by disappearance of yellow color). Wash off watch-glass and sides of beaker, acidify with HCl (1 + 4), evaporate to complete dryness, treat with H_2O acidified with HCl, boil, and filter to remove SiO_2. Dilute filtrate to 300 ml., add 50 ml. of HCl, heat to boiling, and add 10 per cent $BaCl_2$ solution (11 ml. for 1 g. of $BaSO_4$) with constant stirring, at such rate that about 4 minutes is required for running in necessary quantity. (Rate may be regulated by attaching suitable capillary tip to burette containing the $BaCl_2$ solution.) Evaporate to dryness on steam bath, take up with hot H_2O, filter through quantitative filter, wash until free from

chlorides, ignite carefully, and heat to constant weight over Bunsen burner. Calculate percentage of S from weight of $BaSO_4$, using factor 0.1374.

Monosulfide Equivalent.[16] (T)

REAGENT

Standard iodine solution (approximately 0.1 N). Mix 12.7 g. of pure iodine with 25 g. of KI, dissolve in a small quantity of water, filter, and dilute filtrate to 1 liter in a volumetric flask. Standardize against thiosulfate.

Determination.

Dilute 10 ml. of prepared solution (see Preparation of Sample) to approximately 30 ml. with recently boiled and cooled water and titrate with the standard iodine solution until the yellow color just disappears. (There should be no difficulty in determining this end point; if there is, a small crystal of Na nitroprusside may be used, but it must not be added until end point is practically reached, because the blue color, if well developed, cannot be destroyed except by excess of I.) From number of ml. of 0.1 N I solution used calculate percentage of monosulfide equivalent. 1 ml. of 0.1 N I = 0.001603 g. of S as monosulfide equivalent.

Thiosulfate Sulfur. *Iodine Titration Method.*[16] (T)

Continue the titration of the solution used in the determination of the monosulfide equivalent (see above) with the 0.1 N iodine solution, letting the iodine act as its own indicator until a small drop produces a slight permanent coloration. From the number of ml. of 0.1 N iodine solution used calculate the percentage of thiosulfate sulfur. One ml. of 0.1 N iodine = 0.006412 g. of sulfur as thiosulfate.

**Zinc Chloride Method.*[8]

REAGENT

Ammoniacal zinc chloride solution. Dissolve 50 g. of pure $ZnCl_2$ in 500 ml. of H_2O, add 125 ml. of NH_4OH and 50 g. of NH_4Cl, and dilute to 1 liter.

Determination.

To 50 ml. of water in a 200 ml. volumetric flask, add 50 ml. of the prepared solution of lime sulfur (see preparation of sample) in the manner described under total sulfur determination. Add a

slight excess of ammoniacal zinc chloride reagent and dilute to mark. Shake thoroughly and filter through a dry filter. To 100 ml. of filtrate add a few drops of methyl orange or methyl red indicator (see total arsenic determination under Paris green), and exactly neutralize with 0.1 N HCl. Titrate the neutral solution with standard (0.05 N) iodine solution, using a few drops of starch indicator. From the number of ml. of iodine solution used calculate the percentage of thiosulfate sulfur present. One ml. of 0.05 N iodine solution = 0.003206 g. of sulfur as thiosulfate.

***Sulfide Sulfur.**[8]

To 10–15 ml. of water in a small beaker, add, in a manner indicated under total sulfur, a 10-ml. aliquot of the diluted lime-sulfur solution (see preparation of sample). Calculate the amount of ammoniacal zinc chloride (see zinc chloride method for thiosulfate sulfur) necessary to precipitate all the sulfur in the aliquot and add a slight excess. Stir thoroughly, filter, wash precipitate twice with cold water, and transfer filter paper and precipitate to beaker in which the precipitation was made. Cover with water, disintegrate paper with a glass rod and add approximately 3 g. of Na_2O_2, keeping beaker well covered with a watch-glass. Warm on steam bath with frequent shaking until all of the sulfur is oxidized to the sulfate, adding more Na_2O_2 if necessary. Make slightly acid with HCl (1 + 4), filter to remove shreds of filter paper, wash thoroughly with hot water, and determine sulfur in the filtrate as directed under total sulfur.

***Sulfate Sulfur.**

Slightly acidify the solution from the determination of thiosulfate sulfur (zinc chloride method) with HCl (1 + 4), heat to boiling, add slowly and with constant stirring a slight excess of 10 per cent $BaCl_2$ solution, boil 30 minutes, allow to stand overnight, and filter. Calculate the sulfur from the weight of the $BaSO_4$ (factor 0.1374) and report as percentage of sulfate sulfur.

***Total Lime.**[8]

To 25 ml. of the prepared solution (see preparation of sample), add 10 ml. of HCl, evaporate to dryness on steam bath, treat with water and a few ml. of HCl (1 + 4), warm until all the $CaCl_2$ is dissolved, and filter to remove sulfur and any SiO_2 that may be present. Dilute filtrate to volume of 200–250 ml., heat to boiling,

and add a few ml. of NH_4OH in excess, and then an excess of a saturated solution of $(NH_4)_2C_2O_4$. Continue boiling until the precipitated CaC_2O_4 assumes a well defined granular form, allow to stand for an hour, filter, and wash a few times with hot water. Ignite in a platinum crucible over a blast lamp to constant weight and calculate to percentage of CaO.

MINERAL OILS

*Unsulfonatable Residue.

REAGENT

Fuming 38 N sulfuric acid. Mix H_2SO_4 with sufficient fuming H_2SO_4 to obtain a mixture containing slightly more than 82.38 per cent total SO_3. If the fuming acid contains 50 per cent excess SO_3, approximately 100 g. of fuming acid to 140 g. of concentrated acid will be approximately the correct ratio. Determine the exact concentration of mixture and also of a reserve supply of concentrated acid as follows:

Weigh a quantity of the acid in a weighing bulb or pipette having a capillary tube at lower end and a stopcock at upper end and fitted with a Pt wire for suspending on balance. Fill bulb by slight suction, and empty lower end of capillary by closing stopcock simultaneously with withdrawal of the capillary from the acid, wiping off first with a moist and then with a dry cloth. Allow acid to flow down sides of neck of a volumetric flask into cold water. (If a flask about 100 times the volume of the weighing pipette is used, the resultant solution will be approximately 0.5 N.) Wash all traces of the acid into flask, taking precautions to avoid loss of SO_3 fumes. Make to volume and titrate from a burette against standard alkali, using the indicator with which the alkali was standardized. Calculate SO_3 content of both acids and add sufficient concentrated acid to the fuming mixture to bring it to 82.38 per cent (100.92 per cent equivalent, H_2SO_4). The equivalent H_2SO_4 content of this acid must not vary more than ± 0.15 per cent H_2SO_4 from the above figure. Keep acid in small bottles and protect against absorption of moisture from air.

Determination.

Pipette 5 ml. of the oil into Babcock cream bottle 15 cm. (6″) long (either the 9 g. 50 per cent or the 18 g. 30 per cent type).

To reduce viscosity of heavy oils, warm pipette after preliminary draining by drawing it several times through flame of Bunsen burner and drain thoroughly. If greater accuracy is desired, weigh measured charge and calculate its exact volume from weight and sp. gr. of the oil. Add slowly 20 ml. of 38 N H_2SO_4, gently shaking or rotating bottle and taking care that temperature does not rise above 60° C. Cool in ice water if necessary. When mixture no longer develops heat on shaking, agitate thoroughly, place bottle in water bath, and heat at 60°–65° C. for 10 minutes, keeping contents of bottle thoroughly mixed by shaking vigorously 20 seconds at 2 minute intervals. Remove bottle from bath and fill with H_2SO_4 until oil rises into graduated neck. Centrifuge 5 minutes (or longer if necessary to obtain a constant volume of oil) at 1200–1500 r.p.m. Read volume of unsulfonatable residue from graduations on neck of bottle and, to convert to ml., multiply reading from the 9 g. 50 per cent bottle by 0.1 and that from the 18 g. 30 per cent bottle by 0.2. From result obtained calculate percentage by volume of unsulfonatable oil.

MINERAL OIL-SOAP EMULSIONS

*Water.

Weigh out approximately 25 g. of sample of emulsion into a 300–500-ml. Erlenmeyer flask; add 50 ml. of xylene (technical grade is satisfactory), and, to prevent foaming, add a lump of rosin weighing about 5 g. (Do not use powdered rosin.) Distill into a Dean and Stark type distilling tube receiver (see figure 23) and continue distillation until no more water collects in receiver. Allow contents of the tube to cool to room temperature, read the volume of water under the xylene in the tube, and from this volume calculate the percentage of water.

*Total Oil.[17]

Weigh about 10 g. of sample into Babcock cream bottle. Dilute with approximately 10 ml. of hot water and add 5–10 ml. of H_2SO_4 (1 + 1). Set bottle in hot water bath 5 minutes to hasten separation of oil, add sufficient saturated NaCl solution to bring oil layer within graduations on neck of bottle, whirl at rate of 1200 r.p.m. for 5 minutes, and allow to cool. Read volume of oil layer, determine its density, and from these values calculate its

weight and percentage. From this percentage value, deduct percentage of fatty acids (and phenols if present) determined separately, to obtain percentage of oil.

***Soap.**

(Error will result if apparent molecular weight of fatty acids varies appreciably from that of oleic acid.)

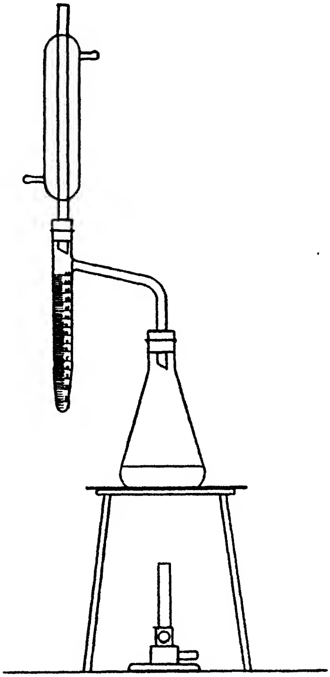

FIG. 23. Dean and Stark distilling apparatus.

Weigh 20 g. of sample into a separatory funnel, add 60 ml. of petroleum benzin, and extract mixture once with 20 ml. and four times with 10 ml. of 50 per cent alcohol. Break emulsion if necessary with 1 or 2 ml. of a 20 per cent solution of NaOH, allowing solution to run down side of separatory funnel, which is then gently twirled and allowed to stand a few minutes. Draw off alcoholic layers and wash successively through petroleum benzin contained in two other separatory funnels. Combine alcoholic extracts in beaker and evaporate on steam bath to remove alcohol. Dissolve residue in about 100 ml. of water made alkaline with

NaOH. Transfer to a separatory funnel, acidify with HCl or H_2SO_4, extract 3 times with ether, and wash ether extracts twice with water. Combine ether extracts, evaporate in weighed beaker on steam bath, and weigh as fatty acids. From weight of fatty acids calculate percentage of soap in sample as Na- or K-oleate.

***Unsulfonatable Residue.**

Using 5 ml. of recovered oil proceed as directed under mineral oil.

***Ash.**

Evaporate 10 g. of sample, or more if necessary, in platinum dish; ignite, and leach charred mass with water. Ignite residue, add leachings, evaporate to dryness, ignite, and weigh. From this weight calculate percentage of ash. Test ash for Cu, Ca, CaF_2, etc.

MARTIN'S SCHEME FOR THE ANALYSIS OF OILS AND OIL EMULSIONS.[18]

Sampling.

Agitate the contents of the drum by vigorous rolling and, if possible, by stirring until thoroughly mixed. Withdraw samples by inserting slowly a wide glass or metal tube to the bottom of the drum. Close the upper end of the tube and withdraw from the drum, transferring the contents to a convenient bottle or container. Sample at least one drum per four of the consignment, taking at least 1 quart per drum.

Content of Solid Matter.

With tar oils or tar oil preparations of the miscible oil type, the content of adventitious solids and solid anthracenoid hydrocarbons is determined by filtering a known weight of about 100 g. of the sample through a weighed filter funnel in the stem of which a small plug of glass wool has been placed. After draining overnight the funnel is reweighed and the weight of solid matter determined.

In some cases the anthracenoid hydrocarbons separating from tar oil preparations on storage may cake to a firm deposit, of which a uniform dispersion cannot be obtained by stirring. If sufficient in amount to warrant examination the drum should be drained through a suitable strainer and the volume of liquid

determined. If less than 95 per cent of the reputed volume it shall be assumed that the tar oil or preparation contains more than 5 per cent solid matter.

The filtered oil or preparation is used for the subsequent examination of neutral oil content, etc.

Neutral Oil Content.

Transfer weighed aliquots (75–100 g.) of the sample to large (1500–2000 ml.) separating funnels with about 500 ml. water. Add 100 ml. of 10 per cent sodium hydroxide solution and shake with about 500 ml. ether (d. 0.730). Stand until a clear ether layer has separated (if the emulsion fails to break sufficiently after standing overnight, add a little (25–50 ml.) saturated sodium chloride solution and rotate gently) and withdraw the lower dilute emulsion or aqueous layer. Re-extract this with successive lots (200 ml. each) of ether until no further oil is extracted. Unite the ether layers, concentrate to about 500 ml. on a water bath, and wash with 1 per cent sodium hydroxide until the ready separation of a colorless aqueous layer occurs. Unite and reserve the aqueous layer and washings (*a*).

Extract the combined ether solutions with successive amounts of 4 per cent hydrochloric acid until the acid layer is no longer strongly colored. Wash the combined acid extracts with successive amounts of ether until the ether layer is colorless. Reserve the combined acid layers (*b*).

Unite the ether washings with the main ether extract and concentrate to 250–300 ml. on a water bath. Add about 20 g. anhydrous sodium sulfate. After 24 hours, filter into a weighed 250-ml. extraction flask and wash the sodium sulfate and filter with ether (dried over anhydrous sodium sulfate), collecting the excess of filtrate in a suitable flask. Distill off the ether on a water bath, adding the excess of filtrate during the process, and remove the last traces of ether by placing the flask in a steam oven and drawing a gentle stream of air over the surface of the oil until the smell of ether is no longer apparent. When cool, weigh flask and oil and calculate the percentage by weight of neutral oil.

NOTE: Certain emulsifiers, e.g. beta-petroleum sulfonic acids, are relatively insoluble in 2 per cent sodium hydroxide, and are not removed by the above procedure. Such emulsifiers are de-

tected by the formation of a definite intermediate layer during ether extraction or by the formation of an emulsion when one or two drops of the extracted oil are shaken with 5 ml. water. The extraction must then be repeated, avoiding the addition of sodium hydroxide in amounts sufficient to give more than a 0.1 per cent solution. The combined ether extracts are finally extracted with 1 per cent sodium hydroxide and the analysis continued as above.

Tar Bases Content.

Add excess of concentrated sodium hydroxide solution to the combined acid washings (*b*), and, when cold, extract with successive amounts of ether until the final ether extract is colorless. Dry the combined ether extracts and determine, as above, the percentage by weight of tar bases.

Tar Acid Content.

Remove, by distillation, the ether dissolved in the combined sodium hydroxide washings (*a*), and transfer the washings to a beaker. Add solid barium hydroxide and place on a boiling water bath until the precipitate (*c*) has coagulated. Add a few drops of barium chloride solution when the non-formation of a further precipitate will indicate a complete removal of fatty acid, resin or sulfonic acid derivatives present as emulsifier. Filter hot through a Buchner funnel with suction. Acidify the filtrate with concentrated hydrochloric acid and, when cold, extract with successive amounts of ether. Dry the combined ether washings with anhydrous sodium sulfate. After 24 hours, filter into a weighed extraction flask and, after removal of the ether, reweigh and calculate the percentage by weight of tar acids.

NOTE: Treatment with barium hydroxide may be omitted if no emulsifier is present, e.g. with straight tar oils, when the tar acids may be extracted direct from the sodium hydroxide washings after acidification.

Examination of Emulsifier.

A heavy barium precipitate (*c*) is indicative of soap, resin or sulfonic acid emulsification, and confirmation may be obtained by warming the precipitate with dilute hydrochloric acid and extraction, when cold, with ether. The combined ether extracts are washed with water until the aqueous layer no longer has an

acid reaction. Dry the ether extract with anhydrous sodium sulfate, filter and evaporate off the ether. The nature of the emulsifier (fatty acid, sulfonated fatty acid, resin or sulfonic acid) may be determined by the usual methods.

The suitability of preparations of the stock emulsion type for use in combination washes is determined by the absence of alkali or ammonium salts capable of yielding insoluble calcium or lead salts when mixed with lime sulfur or lead arsenate. Such ammonium salts are detected by the evolution of ammonia on agitation, while the alkali salts are detected by ashing a small sample of about 10 g. in an evaporating basin after expelling water on a water bath. An ash which dissolves in water to give a solution which shows persistent alkalinity to phenolphthalein after the removal of any lime present by passing carbon dioxide through the solution, indicates the presence of an emulsifier unsuitable for this type of preparation.

Examination of Neutral Oils.

A sufficient amount of neutral oils is obtained by combining the residues from duplicate determinations of neutral oil content.

Specific Gravity.

Determine by means of 25-ml. specific gravity bottle, correcting to 60° F. For details see Standard Methods of Testing Petroleum and its Products, Institution of Petroleum Technologists, 2nd ed., 1929, p. 1.

Viscosity.

Determine with the Redwood No. 1 viscosimeter at 70° F. in accordance with the standard method (I.P.T.L.O. 8).

Boiling Range.

Transfer 100 ml. neutral oil to standard distillation flask and distill according to procedure given in Standard Methods for Testing Tar and its Products, Standardisation of Tar Products Test Committee, 1929, p. 168. To check the temperatures at which 10, 50, and 80 per cent by volume have distilled over, it is sufficient to collect the distillate in a 100-ml. measuring cylinder, recording the temperature of the thermometer when 10, 50, and 80 ml. have collected. The temperature of distillation must be so adjusted

that the distillate collects at the uniform rate of two drops per second.

Typical figures for distillation range determined by this method, when transferred to squared paper, give smooth S-shaped curves, and, in general, at least three points separated as widely as possible are sufficient to define the curve. One of these points is obviously at 50 per cent, while the other two should be as far apart as possible but not on those parts of the curve which approach asymptotically the 0 and 100 per cent distillation ordinates. Further, in the case of the higher temperature, it is better that this should not exceed that (approximately 370° C.) above which pyrolysis becomes important. It is therefore suggested that the temperatures at which 10, 50 and 80 per cent by volume distill be taken to define the boiling range of an oil, but that, as the content of high-boiling fractions is required, these temperatures be expressed as those above which 90, 50 and 20 per cent of the oil distill.

Percentage Unsulfonated Residue.

(*a*) With oils of 60 or more per cent by volume unsulfonated residue. Transfer to a Chancel's sulfurimeter a volume of the neutral oil sufficient to reach approximately to the 30 per cent mark, reading the volume at the upper meniscus. Add twice this volume of concentrated sulfuric acid (d. 1.84) and shake vigorously for 2 minutes, loosening the stopper from time to time to permit the escape of sulfur dioxide. Place the sulfurimeter in a boiling water bath so that the level of the water is above that of the oil-acid mixture in the tube. After about 5 minutes remove and invert the tube at least twice. Release stopper and replace in the water bath. Repeat this process at least twenty times and finally remove the tube, placing it in an upright position. When cold, read off the volume of the supernatant unsulfonated residue and calculate to percentage of initial volume of oil taken.

(*b*) If tar oils or oil of unsulfonated residue less than 50 per cent are present, solid sulfonation products interfere with the method (*a*). With such oils, dilute a known volume of oil in a stoppered measuring cylinder with an equal volume of benzene, add two volumes of concentrated sulfuric acid (sp. gr. 1.84) and shake, cooling under water if the temperature rises above 30° C. Stand

overnight and read off the volume of the residual supernatant layer. Withdraw a sufficient amount and transfer to a Chancel's sulfurimeter, proceeding with the sulfonation by the method (*a*).

NOTE: (1) If x = initial volume of oil taken and y = volume of oil-benzene layer after the preliminary sulfonation; and if a = volume transferred to Chancel's sulfurimeter (in Chancel percentage figures) and b = residual volume of unsulfonated oil, the percentage by volume unsulfonated residue $= \frac{100\,by}{ax}$.

(2) If the residual oil layer in method (*a*) or the oil-benzene layer in method (*b*) is too dark in color to allow the easy demarcation of the oil-acid interface, add a small quantity of water gently from a wash bottle so as to form an intermediate layer.

Dimethyl Sulfate, Percentage Insoluble In.

To one volume of neutral oil in the Chancel's sulfurimeter add two volumes of dimethyl sulfate. Shake vigorously for 1 minute, and stand upright overnight. Read off the volume of the supernatant layer and calculate its percentage of the original volume of oil taken. The temperature should not exceed 20° C.

NOTE. (1) Because of the dark color of the oils it is necessary to read volumes at the upper meniscus.

(2) Old samples of dimethyl sulfates may give unreliable results.

Alkali Content.

This item, which applies only to oils intended for the home preparation of washes by the two-solution method, is included, as the presence of alkali in the oil may lead to faulty emulsification through interaction with the emulsifier. About 10 ml. of the oil are shaken with an equal volume of water which show no alkalinity to phenolphthalein after the addition of 1 ml. N/10 acid.

SOAPS

***Moisture.**

Follow directions given under "Water in mineral oil—soap emulsions" (p. 235) but use a 20 g. sample and a lump of rosin weighing approximately 10 g.

***Potassium and Sodium.**[19]

Dissolve approximately 5 g. of the soap in water, decompose with HCl (1 + 4), filter off the water and wash the fat with cold

water. Ignite in muffle at a low red heat to destroy organic matter. Heat residue on steam bath with 2–5 ml. of HCl and about 50 ml. of H_2O. Transfer to beaker and add NH_4OH dropwise until precipitate formed requires several seconds to dissolve, thus leaving solution but faintly acid. Heat nearly to boiling, and add NH_4OH to precipitate all the Fe, Al, etc. Boil in covered beaker 1 minute; remove, and if no NH_3 is detected by smelling, continue addition, dropwise, until it can be detected. Do not allow precipitate to settle, but stir and pour on filter. Wash immediately with hot water, using, to effect rapid filtration, a fine jet directed around edge of precipitate to cut it free from the paper. Wash precipitate several times, return to original beaker, dissolve with a few drops of HCl, and warm. Reprecipitate the Fe, Al, and P_2O_5 with NH_4OH as directed above; filter and wash until free from chlorides. Evaporate combined filtrates and washings to dryness, heat below redness until NH_4 salts are expelled, and dissolve in hot water. Add 5 ml. of a saturated solution of $Ba(OH)_2$, heat to boiling, allow to settle a few minutes, and determine whether or not precipitation is complete by addition of more of the $Ba(OH)_2$ solution to a little of the clear liquid. When no further precipitate is produced, filter and wash thoroughly with hot water. Heat filtrate to boiling and add NH_4OH (1 + 4) and a 10 per cent $(NH_4)_2CO_3$ solution to complete precipitation of the Ba, Ca, etc. Let stand short time on water bath, filter, and wash precipitate thoroughly with hot water. Evaporate filtrate and washings to dryness, expel NH_4 salts by heating below redness, treat with a little hot water, and add a few drops of the dilute NH_4OH, 1 or 2 drops of the $(NH_4)_2CO_3$ solution, and a few drops of a saturated solution of ammonium oxalate. Let stand a few minutes on water bath and set aside a few hours. Filter, evaporate to complete dryness on water bath, and heat at temperature not exceeding dull redness until all ammonium salts are expelled and residue is nearly or quite white. Dissolve in minimum quantity of H_2O, filter into weighed Pt dish, add a few drops of HCl, evaporate to dryness on water bath, heat at temperature not exceeding dull redness, cool in desiccator, and weigh as KCl plus NaCl. Repeat the heating until constant weight is obtained.

Potassium. *Platinic Chloride Method.*

REAGENT

Platinic chloride solution. Use a Pt solution containing the equivalent of 0.5 g. Pt (1.05 g. H_2PtCl_6) in every 10 ml.

Determination.

Dissolve residue of mixed chlorides, obtained by previous method, with a few ml. of H_2O, acidify with a few drops of HCl, and add excess of $PtCl_4$ solution. Evaporate on water bath to thick paste; treat residue repeatedly with 80 per cent alcohol, decanting through a weighed Gooch crucible or other form of filter, transfer precipitate to filter and wash thoroughly with the 80 per cent alcohol. Dry 30 minutes at 100° and weigh. $K_2PtCl_6 \times 0.16084 = K$. If it is desired to determine the Na, calculate the K to KCl and subtract this from the KCl + NaCl found in preceding paragraph.

SODIUM AND POTASSIUM CYANIDES

***Cyanogen.**

REAGENT

Silver nitrate solution. (0.1 N). Standardize against pure NaCl by titration, using chromate indicator.

Determination.

Break sample into small lumps in mortar (do not grind). Weigh quickly about 5 g. in weighing bottle and wash into 500-ml. volumetric flask containing approximately 200 ml. of H_2O. Add a little $PbCO_3$ to precipitate any sulfides that may be present, dilute to mark with H_2O, mix thoroughly, and filter through dry filter. Transfer 50-ml. aliquot to 400-ml. beaker—caution: do not use pipette for measuring; add 200 ml. of H_2O, 5 ml. of NaOH solution (100 g. to 1 liter of H_2O), and 10 drops of saturated KI solution (or a few crystals); and titrate to faint opalescence with the $AgNO_3$ solution. (In making this titration, it is advantageous to have the beaker over a black surface.) From number of ml. of 0.1 N $AgNO_3$ solution used calculate percentage of CN. The reaction is represented by the equation: $2NaCN + AgNO_3 = NaCN \cdot AgCN + NaNO_3$; hence 1 ml. of 0.1 N $AgNO_3$ solution = 0.005204 g. of CN.

***Chlorine.**

REAGENTS

(*a*) *Ammonium or potassium thiocyanate solution.* 0.1 N. Adjust by titrating against the 0.1 N $AgNO_3$ solution (see previous determination).

(*b*) *Ferric indicator.* A saturated solution of ferric ammonium alum from which brown color has been removed by addition of few drops of HNO_3.

Determination.

Transfer a 50-ml. aliquot of prepared solution (do not use pipette) to beaker, dilute with equal volume of H_2O, add 1–2 ml. of 40 per cent chloride-free HCHO solution, stir well, and let stand 15 minutes. Acidify with 5 ml. HNO_3 (1 + 1), add measured volume of 0.1 N $AgNO_3$ solution, sufficient to give an excess, stir well, filter, wash, and titrate excess of Ag in combined filtrate and washings with the 0.1 N thiocyanate solution, using the ferric indicator. From number of ml. of 0.1 N $AgNO_3$ solution, less number of ml. of thiocyanate solution used, calculate percentage of Cl.

CALCIUM CYANIDE

***Cyanogen.**

REAGENT

Soda-Lead. Dissolve 20 g. of lead acetate in water, dilute to 1 liter, and add 200 g. of chloride-free Na_2CO_3.

Determination.

Place approximately 200 ml. of water in a 500-ml. volumetric flask and carefully dry neck of flask. Weigh approximately 5 g. of sample in weighing bottle and transfer to flask with least possible exposure to air. Wash mixture down into flask and mix by whirling until solution is complete and the small quantity of CaC_2 has been decomposed. Add 25 ml. of the soda-lead reagent, or a quantity sufficient to remove sulfides; close flask with a rubber stopper; and shake thoroughly, preferably for 30 minutes. Dilute to mark, mix and filter through a dry filter. Transfer 50 ml. aliquot to a 400 ml. beaker (do not use pipette) and proceed as directed under the determination of cyanogen in sodium or potassium cyanides, beginning with "Add 200 ml. of water." One ml. of 0.1 N $AgNO_3$ solution = 0.005204 g. of CN. To obtain

percentage of $Ca(CN)_2$ multiply percentage of CN by factor 1.7702.

***Chlorine.**

Transfer a 50-ml. aliquot of the solution prepared according to the directions in the previous paragraph to a beaker (do not use pipette) and proceed as directed under Chlorine in Na and K cyanides.

BORDEAUX MIXTURE

***Moisture.**

(*a*) *Powder.* Dry 2 g. to constant weight at 105–110° C. Report loss as moisture.

(*b*) *Paste.* Heat approximately 100 g. in an oven at 90°–100° C. until dry enough to powder readily and note loss in weight. Powder this partially dried sample and determine remaining moisture in 2 g. as directed under (*a*). Determine CO_2 as directed in the following two paragraphs, both in the original paste and in this partially dried sample. Calculate total moisture by the following formula.

$$M = a + \frac{(100 - a)(b + c)}{100} - d,$$

in which

M = per cent total moisture in original paste;
a = per cent loss in weight of original paste during first drying;
b = per cent loss in weight of partially dried paste during second drying;
c = per cent of CO_2 remaining in partially dried paste after first drying; and
d = per cent of total CO_2 in original paste.

***Carbon Dioxide.**[20]

APPARATUS

Use a 200-ml. Erlenmeyer flask closed with two-holed stopper; in one hole fit a dropping funnel, allowing stem to extend almost to bottom of flask, and through other hole pass outlet of a condenser that is inclined upward at angle of 30° from horizontal. Connect upper end of condenser with a $CaCl_2$ tube, which in turn is connected with a double U-tube filled in middle with pumice

fragments, previously saturated with $CuSO_4$ solution (20 per cent $CuSO_4 \cdot 5H_2O$) and subsequently dehydrated, and with $CaCl_2$ at either end. Connect two weighed U-tubes for absorbing the CO_2, the first filled with porous soda-lime, and the second, 1/3 with soda-lime and 2/3 with $CaCl_2$, placing the $CaCl_2$ at exit end of train. Attach a Geissler bulb, partly filled with H_2SO_4, to last U-tube to show rate of gas flow, and connect an aspirator with Geissler bulb to draw air through apparatus. Connect an absorption tower filled with soda-lime to mouth of dropping funnel to remove CO_2 from the air entering apparatus.

Determination.

Weigh 2 g. of powder or 10 g. of paste into the Erlenmeyer flask and add 20 ml. of H_2O. Attach flask to apparatus, omitting the two weighed U-tubes, and draw CO_2-free air through apparatus until it displaces original air. Attach weighed U-tubes as directed under the previous paragraph, close stopcock of dropping funnel, pour into it 50 ml. of HCl (1 + 4), reconnect with soda-lime tower, and allow the acid to flow into Erlenmeyer flask, slowly if there is much CO_2, rapidly if there is little. When efferescence diminishes, place low Bunsen flame under flask and start flow of H_2O through condenser, allowing slow current of air to flow through apparatus at same time. Maintain a steady but quiet ebullition and a slow air current through apparatus. Boil a few minutes after the H_2O has begun to condense in condenser, remove flame, and continue aspiration of air at rate of about 2 bubbles per second until apparatus is cool. Disconnect weighed absorption tubes, cool in balance case, and weigh. The increase in weight is CO_2.

Copper. **Electrolytic Method.*

Dissolve 2 g. of powdered sample in 25 ml. of HNO_3 (1 + 4), dilute to 100 ml. and electrolyze, using rotating anode and current of about 3 amperes as directed under copper in Paris green.

**Thiosulfate Method.*

Dissolve 2 g. of powdered sample in 25 ml. of HNO_3 (1 + 4), and heat. Without removing the precipitate that has formed, boil off the excess of NH_3, add 3–4 ml. of acetic acid, cool, add 10 ml. of 30 per cent KI solution, and titrate with standard thiosulfate as directed under copper in Paris green.

ORGANIC MERCURIAL SEED DISINFECTANTS

***Mercury.**[21]

REAGENT

Hydrogen peroxide, 30 per cent commonly called "Perhydrol" or "Superoxol."

Determination.

Place 0.5–2.0 g. of sample, depending on quantity of Hg present, in 200-ml. Erlenmeyer flask fitted with air condenser by means of ground-glass joint. Add 10 ml. of H_2SO_4, connect flask to condenser, and rotate in order to bring all the sample into contact with the acid. Add dropwise through condenser tube 3–5 ml. of the H_2O_2 solution, and mix by rotation of flask. After active reaction has subsided, heat over low flame 15–20 minutes, add 5 ml. more of the H_2O_2, and continue heating until all organic matter is destroyed (indicated by a clear solution), adding more H_2O_2 if necessary. Remove flask from heat, allow to cool, wash down condenser, and transfer contents to beaker, filtering if necessary. Dilute to about 200 ml. and destroy excess of H_2O_2 by titration with $KMnO_4$ solution. Precipitate the Hg with H_2S, filter through weighed Gooch crucible, and dry precipitate in oven at 105°–110° C. Extract dried precipitate with CS_2 to remove any precipitated S, again dry, and weigh. From weight of HgS calculate percentage of metallic Hg, using factor 0.8622.

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CHAPTER XV

MICRO ANALYTICAL METHODS

Spray Deposits

Arsenic. **Gutzeit Method.*

Reagents

(*a*) *Stannous chloride solution.* Dissolve 40 g. of As-free $SnCl_2 \cdot 2H_2O$ in HCl and make up to 100 ml. with the same strength acid.

(*b*) *Zinc.* Use 20- or 30-mesh, As-free granulated Zn, that needs no preliminary treatment, or As-free stick Zn either cut into 1-cm. lengths, or melted and cast into pellets in porcelain mold drilled (for example) 9 mm. in diameter and 12.5 mm. deep. Activate the pieces of Zn with HCl (1 + 3), to which has been added 2 ml. of the $SnCl_2$, allowing action to continue 15 minutes. Sort out distinctly inactive or overactive pieces and pour off liquid. Wash Zn free from acid with clear tap H_2O, and rinse with hot H_2O. Select uniformly etched non-pitted Zn and store in suitable receptable. To maintain supply of uniform Zn adopt a system of rotation by withdrawing Zn from the original receptacle until stock is exhausted and storing used Zn in a second receptacle after discarding non-uniform or deeply pitted pieces. Draw Zn from second receptacle after washing it with clear running H_2O. Repeat procedure until pieces are too small for further use.

(*c*) *Ammonium oxalate solution. Saturated.*

(*d*) *Potassium iodide solution.* Dissolve 15 g. of KI in H_2O and dilute to 100 ml.

(*e*) *Sand.* Clean 30-mesh (through 30- but not 40-mesh) white sea sand by washing successively with hot 10 per cent NaOH solution, hot concentrated HNO_3, and hot distilled H_2O. Dry the clean sand.

(*f*) *Mercuric bromide paper.* Use commercial arsenic papers cut from paper of uniform weight and texture into strips exactly 2.5 mm. wide and 12 cm. long. (Uniformity in width and texture of paper are of great importance in this comparison method.

Irregular texture produces irregular impregnation with consequent inaccurate results.) To sensitize, soak strips 1 hour or longer in 3–6 per cent (optimum 5 per cent) solution of filtered $HgBr_2$ in alcohol, according to quantity, character, and activity of Zn used. (Attenuated, unsatisfactory stains, due to over rapid evolution of arsine, can be shortened and intensified by increasing concentration of $HgBr_2$ and vice versa.) If the strips are in sheets, cut off two sides before soaking and leave strips attached at ends. After sensitization remove strips and dry individual ones on glass rods and groups by waving them in the air. Place strips when nearly dry between clean sheets of paper and subject them to pressure long enough to take out bends or curls. Store in dry dark place. (Aging of impregnated strips usually results in markedly fainter and longer stains. Desirable types of stain result from use of impregnated strips not over 2 days old.) When ready for use, cut individual strips off squarely half an inch from one end and insert this end into the narrow tube of apparatus. Handle sheets by the paper attached to either end and cut in half just before use. Strips must be clean and free of any contamination.

(*g*) *Standard arsenic solution.* Dissolve 1 g. of As_2O_3 in 25 ml. of 20 per cent NaOH. Saturate solution with CO_2 and dilute to 1 liter with recently boiled H_2O. One ml. of this solution contains 1 mg. of As_2O_3. Dilute 40 ml. of this solution to 1 liter. Make 50 ml. of the diluted solution to 1 liter and use to prepare standard stains. One ml. of latter solution contains 0.002 mg. of As_2O_3. A solution containing 0.001 mg. of As_2O_3 may also be prepared if desired. Prepare fresh dilute solutions at frequent intervals.

APPARATUS

(*a*) *Generators and absorption tubes.* Use 2-oz. wide-mouthed bottles of uniform capacity and design as generators, and fit each by means of perforated stopper with glass tube 1 cm. in diameter and 6–7 cm. long, with an additional constricted end to facilitate connection. Place small wad of glass wool in constricted bottom end of tube and add 3.5–4 g. of the 30-mesh cleaned sand, as shown in Fig. 24, taking care to have same quantity in each tube. Moisten sand with 10 per cent Pb acetate solution and remove excess by light suction. Clean sand when necessary by

treatment (do not remove sand from tube) with HNO_3 followed by H_2O rinse and suction. Treat with the Pb acetate solution. If sand has dried through disuse, clean and remoisten it as directed. Connect tube by means of rubber stopper with narrow glass tube 2.6–2.7 mm. in internal diameter and 10–12 cm. long, and introduce the clean end of the strip of $HgBr_2$ paper. (A 3 mm. bore allows strip to curl, which results in an uneven stain and poor end point.) Clean and dry tube before inserting the bromide paper. (An ordinary pipe cleaner may be used.)

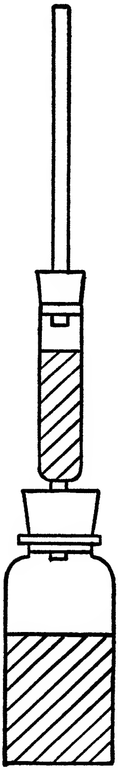

FIG. 24. Gutzeit arsenic apparatus.

(*b*) *Water bath.* Use any constant temperature water bath. If no water bath is available, use any flat-bottomed container of suitable depth and capacity. (A deep water bath is suggested to insure uniform conditions during evolution and absorption of the As.)

Preparation of Sample.

(*a*) *For fresh fruits* (apples, pears or similar products). Weigh and peel representative sample of fruit (1–5 pounds). At blossom and stem ends cut out all flesh thought to be contaminated with arsenical compounds and include with peelings. Place peelings in 1 or more 800-ml. Pyrex Kjeldahl flasks. (As-free Pyrex glassware and "wet ashing" apparatus of Duriron are now available.) Add 25–50 ml. of HNO_3; then add cautiously 20 ml. of H_2SO_4. Place each flask on an asbestos mat with 2-inch hole. Warm slightly and discontinue heating if foaming becomes excessive. When reaction has quieted, heat cautiously and rotate flask from time to time to prevent caking of sample upon glass exposed to flame. Maintain oxidizing conditions in flask at all times during digestion by adding cautiously small quantities of HNO_3 whenever mixture turns brown or darkens. Continue digestion until organic matter is destroyed and SO_3 fumes are copiously evolved. (Final solution should be water-white, or at most a light straw color.) Cool slightly and add 75 ml. of H_2O and 25 ml. of the saturated solution of NH_4 oxalate to assist in expelling

oxides of N from the solution. Evaporate again to point where fumes of SO_3 appear in neck of flask. Cool, and dilute with H_2O to 500- or 1000-ml. in volumetric flask.

(*b*) *For dried fruit products.* Prepare sample by alternately grinding and mixing 4–5 times in food chopper. Place 35–70-g. portions in 800-ml. Kjeldahl flasks, and add 10–25 ml. of H_2O, 25–50 ml. of HNO_3, and 20 ml. of H_2SO_4. Continue digestion as directed in (*a*). Dilute digested solution to 250 ml.

(*c*) *For small fruits, vegetables, etc.* Use 70–140 g. of sample and digest as directed under (*a*) and (*b*).

(*d*) *For materials other than* (*a*), (*b*), or (*c*). Digest 5–50 g. according to degree of dryness and amount of As expected, as directed under (*a*) and (*b*). Dilute to definite volume dictated by circumstances.

(*e*) *For products containing stable organic As compounds, products liable to yield incompletely oxidized organic derivatives that inhibit arsine evolution, or products that are otherwise especially difficult to digest.* Shrimp, tobacco, oils, and sometimes other products require special treatment to complete oxidation of organic As to inorganic As_2O_5, or to destroy organic interference previous to As determination. (For details consult references 2, 3, 4, 5.)

Dilute the As solutions obtained by these special methods of preparation to definite volume.

Isolation of Arsenic.

Isolate the As when interfering substances are present in digests (pyridine from tobacco), or when samples contain excessive amounts of salts, or H_2SO_4 from digestions, before making determinations. Consult reference (2), or use trichloride distillation of bromate method.

Determination.

Determine the acid HCl or H_2SO_4 according to previous treatment, by titration if necessary, in definite volume of sample solution. Place aliquots containing 0.01–0.03 mg. of As_2O_3 (0.020–0.025 mg. is optimum) and not larger than 30 ml. in Gutzeit generators. If arsenic in aliquot taken is found to be outside the limits specified, repeat with proper aliquot. If aliquot contains only HCl, add sufficient HCl to make total volume of 5 ml.; if it contains H_2SO_4, add sufficient 25 per cent As-free NaOH

solution (keep in As-free Pyrex) exactly to neutralize it and add 5 ml. of HCl, or add sufficient HCl to the H_2SO_4 in aliquot to make total volume of 5 ml. Cool when necessary and add 5 ml. of the KI reagent and 4 drops of the $SnCl_2$, reagent (*a*). Prepare standards corresponding to 0.010, 0.020, and 0.030 mg. of As_2O_3 from reagent (*g*). Since the standards must contain same kind and amounts of acid as samples, add 5 ml. of HCl, or H_2SO_4 and HCl (total 5 ml.) according to prior treatment of unknown. If the H_2SO_4 has been neutralized, add an equivalent quantity of As-free Na_2SO_4 to standards. Mix, and allow to stand for 30 minutes at not less than 25° C. or 5 minutes at 90° C. Dilute with H_2O to 40 ml.

Prepare generator as directed under apparatus and center strip of $HgBr_2$ paper carefully in the narrow tube. According to activity of the Zn, add to each of standards and samples 10–15 g. of activated stick Zn or 2–5 g. of granulated Zn and add the same quantity to each generator. Equalize as far as possible surface area of Zn exposed in standard and sample. If sheets of strips are used, prepare sample and standard strips from same strip-group.

Immerse apparatus to within 1 inch of top of narrow tube in water bath, which is kept at constant temperature of 20°–25° C., and allow evolution to proceed for 1.5 hours. Remove strip and average length of stains on both sides in mm. Plot graph of standard strips on cross-section paper, using length in mm. as ordinate and the mg. of As_2O_3 as abscissa. (Preparation of standard graph averages errors of individual standards. Reading strip from such a graph is considered more convenient and accurate than comparing strips themselves.) Locate length of unknown strip on standard graph and read off on abscissa quantity of As present. Report only to third decimal as grains of As_2O_3 per pound. Take smaller or larger aliquots when stain is longer or shorter than highest or lowest standard, respectively. Grain/lb. $\times$ 143 = p.p.m.; p.p.m. $\times$ 0.007 = grain/lb.

Frequent blanks should be made. With reagents of suitable quality, blanks should not show more than 0.001 mg. of As_2O_3.

Bromate method. (T)

(Applicable to determination of arsenic in plants and food products where a sample of convenient size for digestion will yield at least 0.005 grain (0.324 mg.) of As_2O_3.)

REAGENTS

(*a*) *Ammonium oxalate-urea solution.* To saturated H_2O solution of NH_4 oxalate add 50 g. of urea per liter.

(*b*) *Hydrazine sulfate-sodium bromide solution.* Dissolve 20 g. of hydrazine sulfate and 20 g. of NaBr in 1 liter of HCl (1 + 4).

(*c*) *Sodium chloride.* Commercial salt, uniodized.

(*d*) *Standard potassium bromate solution.* Dissolve 0.1823 g. of $KBrO_3$ in H_2O and dilute to 1 liter. 1 ml. = 0.005 grain of As_2O_3. Standardize by titration against the standard As_2O_3 solution (*e*), making titration at 90° C. and in presence of about 100 ml. of H_2O and 25 ml. of HCl, in order to simulate conditions under which samples will be titrated. 1 ml. of the bromate solution should be equivalent to 1 ml. of As_2O_3 solution.

(*e*) *Standard arsenious oxide solution.* Dissolve 0.3241 g. of As_2O_3 in 25 ml. of 10 per cent NaOH, make slightly acid with H_2SO_4 (1 + 6), and dilute with H_2O to 1 liter.

DISTILLING APPARATUS

The distilling apparatus consists of 800-ml. Kjeldahl flask (A), distilling tube (B), and 300-ml. Erlenmeyer flask (C).

To prepare distilling tube, bend 10–15 mm. glass tube to acute angle of about 70°. Draw the longer arm, which is 15–20″ long, down to orifice of 3 mm. Fit shorter arm (4″) with No. 7 rubber stopper, which has previously been boiled in 10 per cent NaOH for 15 minutes, and then in HCl for 15 minutes, in order to remove most of the sulfur compounds which might be distilled and react with the bromate solution. The complete set-up is illustrated in figure 25.

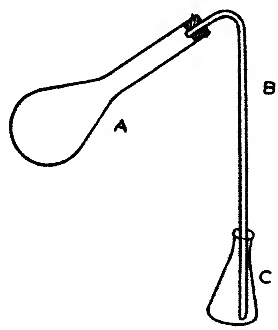

FIG. 25. Bromate distillation apparatus.

Preparation of Sample.

Introduce suitable sample containing 0.005 grain (0.324 mg.) or more of As_2O_3 into an 800-ml. Kjeldahl flask. Proceed with acid digestion as directed under Gutzeit arsenic determination, with following exception: Add exactly 20 ml. of H_2SO_4, or (rarely), if material is difficult to digest, exactly 25 ml. at beginning of digestion. After digestion is complete, add 50 ml. of H_2O and

25 ml. of the NH_4 oxalate-urea solution, and boil until white SO_3 fumes extend up into neck of flask to decompose oxalates and urea completely. (Volatile intermediate products may titrate with bromate. If heat available is insufficient to decompose these substances, it is preferable to evaporate to fumes with H_2O alone. Hydrazine sulfate will destroy small amounts of oxides of nitrogen.)

Isolation.

Add 25 ml. of H_2O to digested solution in the Kjeldahl flask and cool to room temperature. Put 100 ml. of H_2O into flask C. Add to solution in Kjeldahl flask 20 g. of NaCl and 25 ml. of the hydrazine sulfate-sodium bromide solution and connect distilling tube. Heat Kjeldahl flask over small well-protected flame, and distill into the H_2O in Erlenmeyer flask. (Heating is not intended to boil solution but to bring about evolution of HCl gas, which carries over the $AsCl_3$ with it. Absorption of evolved HCl gas by H_2O causes rise in temperature, which indicates progress of distillation.) Adjust flames so that temperature of distillate solution will rise to 90° C. in 9–11 minutes and then discontinue distillation. (Residual mixture in flask should not be less than 55 ml.) If distillation proceeds further, or larger quantity of H_2SO_4 than that specified is used in the digestion, SO_2 is distilled, which is titrated as As.

Determination.

Titrate distillate at once with the bromate solution, using 3 drops of methyl orange indicator. (Single drops of indicator, reagent (*d*), total As in Paris green, p. 210, but not exceeding 3, may be added during titration as the red color fades.) Towards end of titration add the bromate solution very slowly and with constant agitation to prevent local excess. The end point is reached when a single drop of the bromate just destroys the final tinge of red color. Use Erlenmeyer flask containing clear H_2O for comparison. (End point must not be exceeded as action of indicator is not reversible and back titrations are not reliable. At the proper end point, the red color produced by 2 additional drops of methyl orange indicator should persist for at least 1 minute.) Correct results for volume of bromate used in blank run (digest 5 g. of pure sucrose) with the same reagents (same quantities) and regular distillation procedure. (The blank titration should

not exceed 0.7 ml. of bromate solution. The method is accurate down to variations in blank, which should not exceed 0.1 ml. when chemicals from same lot are used.) Should blank titration be high or variable, test individual reagents for purity by bromate titration and discard unsatisfactory ones. Test the H_2SO_4 by bringing 20 ml. to boil, cooling, diluting with H_2O to 100 ml., adding a little HCl, and titrating while hot. It probably will furnish most of the blank. Select rubber stoppers carefully as they are often the source of unsatisfactory blanks.

If high results, due to SO_2 produced during distillation, or other reducing substances, are suspected, dilute titrated distillate to definite volume and redetermine the As in aliquot by Gutzeit method. A positive test for sulfates in an aliquot of the titrated distillate indicates contamination with reduced S compounds and a necessity for check on the As. All glass apparatus will reduce blanks to minimum.

NOTE: The choice between the Gutzeit and the bromate method for the determination of arsenic depends upon the circumstances, the type of sample, and the amount of arsenic present. Both methods are empirical, and neither is adapted to the casual determination of arsenic in one or two samples. In the hands of an experienced analyst, routine analyses by either method can be highly accurate. The Gutzeit method has two advantages over the bromate distillation: large numbers of determinations may be made in a short time—it is not difficult to carry out 120 or more determinations per working day—and secondly, it will determine extremely small amounts of arsenic. Against these points, however, must be weighed the following: The color of the impregnated paper strips is often very difficult to read with any degree of accuracy, and the method in general tends to be difficult for the average analyst.

The bromate distillation method, on the other hand, is equally empirical as normally used, and does not determine such small quantities of arsenic (1 ml. of the bromate solution as ordinarily made up = 0.005 grain of As_2O_3). However, the reproducability and convenience of the bromate method are such that it has replaced the Gutzeit method in most laboratories at the present time.

Lead on Fresh Fruits and Vegetables.[a] *Preparation of Sample.*

(*a*) *Ashing.* Weigh and peel as large a sample of fruit as is convenient (500–2000 g.). Cut out all flesh at stem and blossom ends thought to be contaminated with arsenic. Place peelings and ends in porcelain dish or casserole and dry in oven at 105°–110° C. When dry, ash in a furnace at a temperature not exceeding 500° C. Ash should be free from carbon. Cool, cover container with watch glass, add 25 ml. of water and cautiously add 15–25 ml. of HCl. Heat on steam bath. If solution does not become clear, evaporate to dryness, add HCl again and repeat evaporation to dehydrate silica. Take up with 15 ml. HCl, heat and filter with suction through a fritted glass filter. Leach insoluble material on filter with a few ml. of hot HCl and hot 40 per cent NH_4 acetate solution, followed by hot water. Transfer filtrate to volumetric flask and make to mark when cool.

(*b*) *Acid digestion ("wet ashing").* Follow directions given for preparation of sample for Gutzeit arsenic determination, (*a*) or (*c*).

(*c*) *Rapid "washing method."*

REAGENTS

(*a*) *NaOH,* 30 per cent.

(*b*) *Sodium oleate solution,* 10 per cent. To 45 ml. of 30 per cent NaOH and 400 ml. of water in a 1.5-liter beaker add slowly while heating and stirring 90 g. of oleic acid. Heat on steam bath until clear; cool and dilute to 1 liter.

Weigh out 10 or more apples or pears, and pull or cut out stems with a narrow-bladed knife so as to expose junction of stem and fruit to the action of the solvent. Trim off sepals (dried residue of blossom) so that solvents have unimpeded entrance to an egress from calyx cup. Allow stems and sepals to fall into a large funnel inserted into neck of 500 ml. volumetric flask. To 25 ml. of the 30 per cent NaOH (reagent *a*) in a 600-ml. beaker, add 175 ml. of water and 25 ml. of 10 per cent Na oleate (reagent *b*),

[a] In the 1940 edition of "Official and Tentative Methods of Analysis" some 16 pages are given over to procedures adapted to the determination of small quantities of lead in foodstuffs and related products. It is obviously impossible to present such an exhaustive discussion here, so that only typical methods for the determination of lead on fresh fruits and vegetables will be given. For further details the reader is referred to the "Official and Tentative Methods of Analysis." [1]

and bring to a gentle boil. Have ready in a wash bottle 250 ml. of hot HCl (3 + 97). Impale each fruit in turn upon a pointed glass rod, immerse in the alkaline solution, with occasional rotation until skin begins to check, then remove to funnel and rinse with a stream of the hot acid, being careful to flush out stem and calyx ends thoroughly and to allow the rinse acid to flow over stems and sepals in the funnel. When all fruit has been thus treated, cool the alkaline solution and add it through the funnel to the acid solution in flask. Rinse the beaker and funnel with any remaining acid and with water, using the entire 250 ml. of rinse acid. Cool, add 25 ml. of HNO_3, and make to volume when again cool. Determine lead on a suitable aliquot of this solution by one of the methods described below,[b] filtering the solution through a dry filter paper before use. Use only clear filtrate.

A. Electrolytic Determination. (T)

REAGENTS

(*a*) *Standard lead solutions.* Dissolve 20–50 g. of C.P. $Pb(NO_3)_2$ in a minimum of hot water and cool with stirring. Filter crystals with suction on a small Buchner funnel, redissolve, and repeat the crystallization. Dry crystals at 100°–110° C. to constant weight. Cool in a desiccator and preserve in a tightly stoppered bottle. (The product has no water of crystallization and is not appreciably hygroscopic.) Prepare stock solution containing equivalent of 2 mg. of Pb (3.197 mg. of $Pb(NO_3)_2$) per ml. in 1 per cent HNO_3. Prepare weaker dilutions with 1 per cent HNO_3 as needed. Do not store for periods over one year.

[b] The three methods for the determination of lead given in following pages are intended to be typical, rather than specific. The accurate determination of such extremely small quantities of any element necessitates great care and a high degree of perfection in chemical technique. All reagents should be carefully checked for the possible presence of lead, and all apparatus should be scrupulously clean. The methods presented are included for use only to determine lead in spray deposits, where there are no other metals (other than those ordinarily in sprays themselves) present. The analysis of other food products, such as canned goods, where the sample may contain tin, for example, presents difficulties, and methods specifically adapted for such cases should be used. Such methods may be found in the "Official and Tentative Methods" of the Association of Official Agricultural Chemists.[1] The choice between the three methods listed below rests with the user. It has been the experience of the author that the sulfide method (*C*) is the most rapid, and the electrolytic method (*A*) the most accurate.

(*b*) *"Stripping reagent."* To 20 ml. of saturated sodium acetate add 10 ml. of glacial acetic acid and make to 100 ml.

(*c*) *Potassium iodide solution,* 2 per cent. Prepare as frequently as necessary to prevent the formation of a starch-iodine color when mixed with reagent (*b*) in the proportion of 4 parts of (*b*) to 1 part (*c*).

(*d*) *Starch solution.* Make up 1 g. of soluble starch to 200 ml.

(*e*) *Sodium thiosulfate.* Approximately 0.1 N stock. Dissolve 24.8 g. of $Na_2S_2O_3 \cdot 5H_2O$ in 1 liter of CO_2-free water and allow it to stand (preferably for two weeks) before use. Prepare approximately 0.001 N and 0.005 N solutions by diluting the stock solution in exact ratios of 1/100 and 1/20 with CO_2-free water. Standardize these solutions against a standard lead solution, following the procedure as given under "Electrolysis" following. Use sufficient standard solution to yield from 0.2 to 1.0 mg. of Pb for the 0.001 N thiosulfate, and from 1–5 mg. of Pb for the 0.005 N dilution. Subtract the anode blanks, and take as the thiosulfate factor the average number of mg. of Pb equivalent to 1 ml. of the thiosulfate solutions. Make fresh dilutions daily, and check the Pb factor at least every month.

(*f*) *Citric acid solution.* Dissolve 50 g. of lead-free citric acid in water and make to 100 ml.

(*g*) *Diphenylthiocarbazone* (dithizone). Dissolve approximately 1 g. of the commercial reagent in 50–75 ml. of $CHCl_3$ and filter if insoluble residue remains. Shake out in separatory funnel with four 100 ml. portions of metal-free NH_4OH (1 + 99). Dithizone passes into the aqueous phase to give orange colored solution. Filter aqueous extracts through a pad of cotton into large separatory funnel. Acidify slightly with dilute HCl and extract precipitated dithizone with two or three 20 ml. portions of $CHCl_3$. Combine the extracts in a separatory funnel and wash 2 or 3 times with water. Draw off into a beaker and evaporate the $CHCl_3$ with gentle heat on steam bath, avoiding spattering as solution goes to dryness. Remove last traces of moisture by heating for an hour at not over 50° C. in vacuo. Store the dry reagent in the dark in a tightly stoppered bottle. Make up reagent solutions for extraction to contain 100, 50, and 10 mg. per liter in freshly distilled $CHCl_3$ and store in the dark in refrigerator.

APPARATUS

While a satisfactory electrolytic apparatus may be assembled from parts secured by the user, it is strongly recommended that an apparatus specifically designed for electrolytic determination be purchased. Such outfits are available in a wide range of prices. A satisfactory apparatus such as that illustrated in figure 26 permits the current to be reduced to 75 milliamperes, and is so designed to allow the solution to be heated. The electrodes consist of a 45-mesh sandblasted Pt-gauze cylindrical anode, approximately 1″ × 5/16″, and 4″ long overall, and a cathode of 18-gauge Pt wire wound in spiral form. For larger amounts of lead (over 5 mg.) a cylindrical anode 2″ × 1/2″ or larger is convenient. Some form of siphon should be provided so that the electrolyte can be replaced by distilled water without interrupting the current when the deposition of lead is complete.

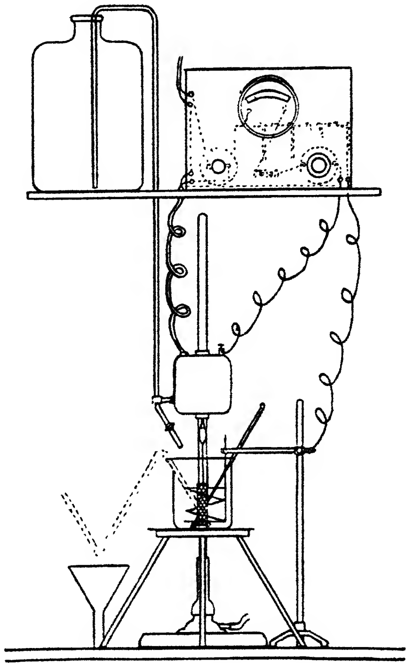

FIG. 26. Electrolytic apparatus.

Separation of Lead.

Transfer a suitable aliquot of the solution containing the lead to a 300-ml. short-stemmed separatory funnel and add citric acid reagent (*f*) equivalent to 10 g. of citric acid. Make slightly alkaline to litmus, keeping solution cool, and allow to stand 2–5 minutes. Add 5 ml. of 10 per cent KCN or NaCN solution, and check the pH of the solution by adding a drop of thymol blue indicator and observing the color of the drop. (The pH should be 8.5 or above, blue green to blue with thymol blue.) Immediately extract with 20-ml. portions of dithizone, using weaker solutions unless exceptionally large quantities of lead are present. Shake for 10–15 seconds, allow layers to separate, and note color of

$CHCl_3$ phase. The Pb-dithizone complex is red, but may be masked by excess green dithizone, giving intermediate hues of purple or crimson. (The color of the $CHCl_3$ extract gives an indication of the amount of lead present and the completeness of the extraction.)

Draw off $CHCl_3$ layer into a 125-ml. short-stemmed separatory funnel containing 25–30 ml. of water made ammoniacal with one drop of NH_4OH (sp. gr. 0.90). Continue extraction of the solution in the larger funnel until two successive extracts with small portions of the weaker dithizone solution show the negative green (not bluish or purple) color, combining the extracts in the smaller separatory funnel. Shake, allow layers to separate, draw $CHCl_3$ fraction into another small separatory funnel, and repeat washing process as before. Draw off $CHCl_3$ fraction as cleanly as possible into 100- or 150-ml. beaker and pass small portion of dilute dithizone solution through funnels in succession as a rinse. Add these to beaker and evaporate $CHCl_3$ with gentle heat on steam bath. Take up dry residue with 3–4 ml. HNO_3, and heat by swirling over low flame. Dilute to approximately 25 ml. and continue heating 1–2 min. to drive off oxides of N. Neutralize with NH_4OH (litmus paper), dilute nearly to capacity of beaker, add 1 ml. of water-white HNO_3 per 100 ml. of solution and electrolyze.

Electrolysis.

Immediately before electrolyzing bring anode to red heat in oxidizing flame of burner. (A variable titration blank is obtained if anode is not heated just before determination, due possibly to film of oxygen adsorbed on anode and activated during electrolysis. Heating reduces and renders constant this "oxygen blank." With small anode it will be 0.07–0.1 ml. of 0.001 N thiosulfate and with larger electrode proportionately larger. The blank for a particular anode should be determined from the average of a series of determinations conducted on pure reagents.)

In all determinations the sample at this point is contained in a volume of 100–125 ml. of 1 per cent HNO_3 (with the large anode a volume of 200 ml. is convenient). Place beaker (100–150-ml. for small and 250-ml. for large anode) in position, making sure electrodes are well covered with solution, and start motor. Heat to 60°–70° C., and add approximately 100 mg. of $K_2Cr_2O_7$ to keep

solution in oxidized state and repress formation of nitrites, especially when organic matter is present. Start current and electrolyze with 75 milliamperes for 20 minutes at 70°–80° C. Use 100–150 milliamperes for larger anode. Remove flame, insert siphon in beaker, and start stream of distilled H_2O playing directly on anode. Start siphon, taking care to keep level of liquid above deposit. (A convenient siphon can also be made by connecting an inverted V-shaped tube to an ordinary water-pump.) The acid is entirely removed when current falls to zero. Turn off motor, electrolytic current, and rinse water; remove anode from the chuck and give it a final rinse with H_2O.

Titration of PbO_2.

Dissolve the deposit from the anode in 4–5 ml. of the "stripping reagent" (*b*) + 1 ml. of the KI reagent (*c*), contained in a flat-bottomed vial of such size that the solution just covers the anode. Add a few drops of the starch solution (reagent *d*), and titrate the liberated iodine with 0.001 N thiosulfate solution (reagent *e*) in the vial, using the anode as the stirrer and sighting downward through the solution in the vial to determine the delicate endpoint. (If the quantity of Pb is seen to be large (1–5 mg.), use 0.005 N thiosulfate (reagent *e*) and double the amount of reagents (*b*) and (*c*) used. With larger electrodes even larger amounts of reagents may be used.) No yellow insoluble PbI_2 should form upon the addition of reagents (*b*) and (*c*); if it does, add more of the sodium acetate. The deposit should dissolve completely and almost immediately. To determine the amount of Pb, subtract the anode and reagent blanks from the total titer and multiply by the factor for the thiosulfate, determined as described under reagent (*e*).

$$PbO_2 + 4HI \rightarrow I_2 + PbI_2 + 2H_2O$$

B. Colorimetric Dithizone Determination. (For quantities of Pb up to 0.200 mg.) (T)

(*h*) *Ammonia-cyanide mixture.* To 100 ml. of 10 per cent recrystallized, phosphate-free KCN or NaCN in a 500-ml. volumetric flask add sufficient redistilled NH_4OH to introduce 19.1 g. of NH_3 and make the volume with redistilled water. (Strength of redistilled NH_4OH can be determined by specific gravity or by titration.)

For other reagents see "Electrolytic Determination" above.

Separation.

Proceed as outlined under "Separation" under "Electrolytic Determination" above, but do not wash the dithizone extracts with dilute NH_4OH, but run directly into a smaller separatory funnel containing 25 ml. of 1 per cent HNO_3 (free from nitrous fumes). When extraction is complete, shake combined extracts in smaller separatory funnel and draw off green dithizone layer into another separatory funnel containing a further 25-ml. portion of 1 per cent HNO_3. Shake, allow layers to separate, and discard the $CHCl_3$ fraction. Filter acid extracts containing Pb in succession through small pledget of wet cotton inserted in stem of small funnel, into 50-ml. flasks or glass-stoppered cylinder, using second acid extract to wash out funnel in which first acid extraction was made. Make up any slight deficiency in volume with 1 per cent HNO_3, and compare with standards as described below.

Color Comparison.

Prepare 10 standards covering in equal steps the range in which it is desired to work, using a standard lead solution (reagent *a*), 1 ml. of which represents some simple fraction or multiple of 1 microgram (0.001 mg.) of Pb. Measure the amounts representing the various steps of the range into a series of separatory funnels and add the pure 1 per cent HNO_3 so that the total volume is always 50 ml. Add 10 ml. of the ammonia-cyanide mixture (reagent *h*) and mix. The resultant pH will be approximately 9.7. Immediately add the appropriate volume of standard dithizone, which depends on the range to be covered as indicated in the following table:

Range of Lead Concentration, Micrograms	Dithizone Concentration, Mg./l.	Volume of Dithizone, Ml.	Cell Length, Inches
0–5	4	5	2
0–10	4	10	2
0–20	8	10	1
0–50	8	25	1
0–100	10	30	½
0–200	20	30	½

Shake for 1 min. and draw off lower layers into a series of tubes or vials and arrange in order. For the lower ranges, up to 20 micrograms of lead, matching is best done by viewing longitudinally in small flat-bottomed vials about 3″ in length. For higher concentrations, the depth of column of liquid must be reduced.

For the determination, place an aliquot part, or all of the 50 ml. of 1 per cent HNO_3 in which the Pb has been isolated (see "Separation" above), in a separatory funnel and, if an aliquot has been taken, make to 50 ml. with the 1 per cent HNO_3. Add 10 ml. of the ammonia-cyanide mixture (*h*) and mix. Immediately develop the color by shaking 1 min. with the proper amount of standard dithizone. Draw off lower layer into tube or vial similar to those used with standards and compare. If range is exceeded, repeat with smaller aliquot. Interpolation between steps of the various ranges can readily be made. If an aliquot of the 50 ml. of the 1 per cent HNO_3 in which the Pb was isolated is taken, subtract only a corresponding amount of the total reagent blank from the amount of Pb found.

C. Photoelectric Sulfide Determination.[6]

REAGENTS

(*i*) *Ammonia-cyanide-citrate mixture.* To 913 ml. of NH_4OH add 5 g KCN and 31.3 g. Pb-free citric acid. When solution is complete, make to 1 liter with water.

(*j*) *Sodium sulfide solution.* 10 per cent solution.

APPARATUS

Any commercial photoelectric colorimeter may be used for this determination, or if none is available the apparatus described by Frear and Haley [6] may be constructed. This consists of a source of light, in this case a 6-volt automobile headlight bulb of 32–32 candlepower, both filaments of which are connected in series to a 12-volt storage battery, with a suitable rheostat included in the circuit to vary the intensity of the light; a photoelectric cell, the most convenient type of which has been found to be the Weston Photronic cell 594, connected to a microammeter with a total capacity of 100 microamperes. To complete the apparatus a case is necessary to hold the photoelectric cell and light source in fixed positions, and to allow a Nessler tube approximately 25 cm. long and 3 cm. in outside diameter to be placed between the two.

A sketch of the apparatus is shown in Figure 27. The relatively intense source of light may, in some cases, develop too great heat, which may be dissipated by a water jacket placed around the socket. A hole 1 mm. smaller in diameter than the outside diameter of the Nessler tube is made in the false bottom of the light chamber directly over the center of the Photronic cell. A tight fit at this point excludes all extraneous light from the cell, and no door is necessary at the front of the apparatus. A photograph of the completed apparatus is shown in Figure 28.

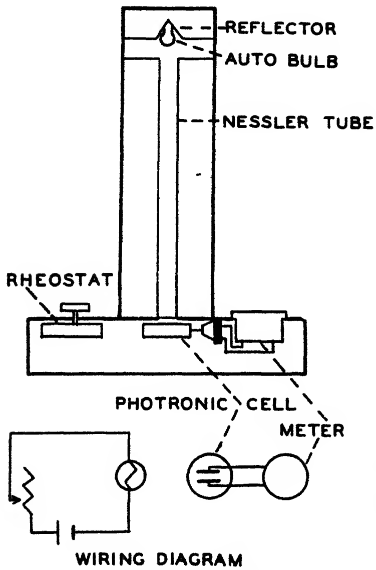

FIG. 27. Diagram of the Frear-Haley photoelectric colorimeter.

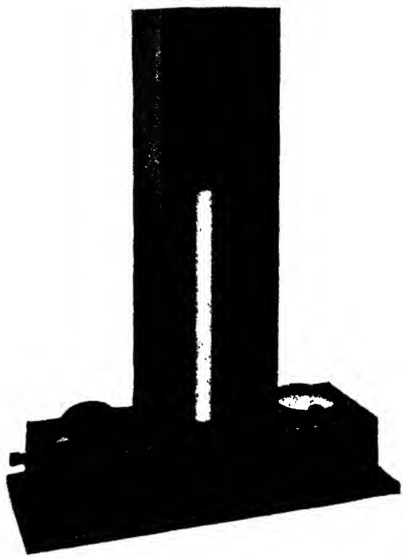

FIG. 28. Photoelectric colorimeter (Frear and Haley).

Determination.

A suitable aliquot of lead solution (containing up to 0.3 mg.), prepared by one of the methods outlined previously (ashing, wet ashing, or "washing"), is placed in a 150-ml. beaker, diluted to approximately 50 ml. with water and when cool made alkaline with 40 ml. of ammonia-cyanide-citrate reagent (*i*). When cooled to room temperature, this solution is placed in the Nessler tube, made to 100 ml. with water and thoroughly mixed. The tube is now placed in position in the colorimeter, and the light intensity adjusted so that the microammeter reading is at the

maximum of the instrument. Six drops of the sodium sulfide reagent (*j*) are added, the solution thoroughly mixed, replaced in the colorimeter, and the second reading of the microammeter taken. The amount of lead is read from a chart prepared as follows: Known amounts of standard lead solution (reagent *a* above) are measured into suitable containers and treated in exactly the same way as the samples on which determinations are made. (This includes the addition of all reagents, and, if the treatment of the samples included acid digestion, the use of 0.25–0.5 g. of sucrose to simulate the organic matter present in the unknown samples.) These standard solutions are taken to cover the range of the determination, from 0 to 0.3 mg. of Pb, and the determinations are made in the photoelectric colorimeter in the manner described above. A typical calibration curve is shown in Figure 29. Any photoelectric colorimeter may be used for the

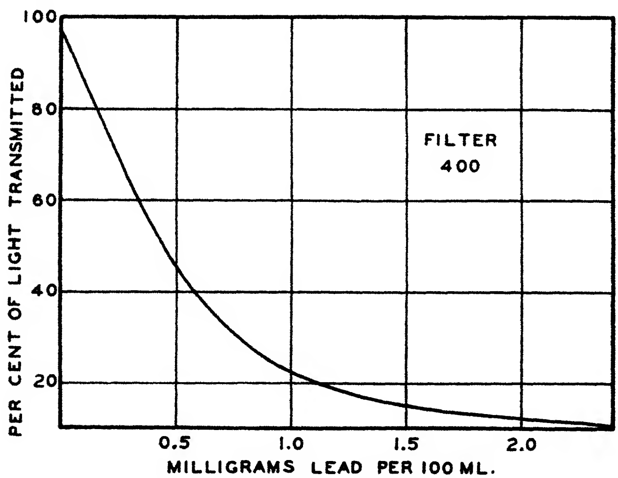

FIG. 29. Typical calibration curve for lead in photoelectric colorimeter (sulfide method).

determination, by slightly modifying the procedure, and it is recommended that a light filter transmitting in the neighborhood of 400 millimicrons be used for greatest sensitivity.

Copper in Spray Deposits.[7] *Method A.*

When copper is present in the sample in amounts greater than 2 mg., the most accurate and convenient method of determination

is by direct weighing after electro-deposition on platinum electrodes. The determination of small quantities (under 50 mg.) is considerably more difficult, however, than the ordinary electrodeposition as followed in the case of copper ores or alloys. The procedure found satisfactory for leaf samples which have received one or more applications of copper sprays is as follows:

A sample of from 2–20 g. of the dried material is ashed at a temperature not exceeding 450° C. The ash is dissolved in nitric acid (1 + 1) and transferred to a 150-ml. beaker. To this solution are added 10 ml. of a saturated solution of ammonium nitrate and 1 g. of urea, and the volume is made up to about 100 ml. The electrolysis is then carried out in the usual manner, using a platinum-gauze cathode and a rotating platinum loop anode. The current between the electrodes must be much lower than is usually recommended in the methods for the electrolytic deposition of copper described in the literature, and should not exceed 0.15 ampere. Currents in excess of this amount will cause the deposition of copper oxide. The time required for complete deposition is a function of the quantity present, but for the amounts normally present on leaf samples 20 minutes is usually sufficient.

Method B.

When the total quantity of copper in the sample is less than 2 mg., it is usually not possible to weigh the metal directly with sufficient accuracy. Samples of fruits and small areas of synthetic surfaces sprayed in the laboratory usually bear less than 1 mg., and hence require a method of analysis sensitive to smaller amounts.

The solution containing the copper is freed from organic matter, if the latter is present, by digestion with sulfuric and nitric acids.

The solution, free from organic matter, is neutralized with concentrated ammonium hydroxide, and about 10 ml. are added in excess. The mixture is then boiled for a few minutes, allowed to stand for 30 minutes, filtered through a fast filter paper, and washed. The entire filtrate, or an aliquot of it, is transferred to a Nessler tube, 25 ml. of concentrated ammonium hydroxide are added, and it is made to a volume of 100 ml. The tube is then placed in a photoelectric colorimeter of the type described by Frear and Haley,[6] the light intensity is adjusted to the maximum

scale reading, 1 ml. of a 1 per cent solution of sodium diethyl dithiocarbamate is added, the solution is stirred, and a second reading is taken. By calibrating the instrument with known amounts of copper, the reading on the microammeter or galvanometer may be converted directly into milligrams of copper. A typical calibration curve is shown in Figure 30. If an Evelyn or similar photoelectric colorimeter is used, a light filter transmitting in the 440 millimicron band should be used.

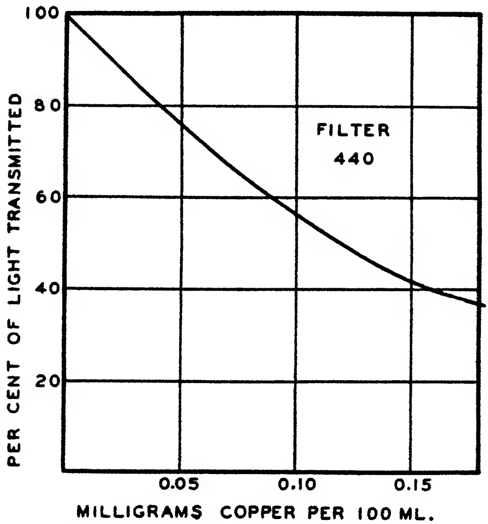

FIG. 30. Typical calibration curve for copper in photoelectric colorimeter (sodium diethyl dithiocarbamate method).

Nicotine in Spray Deposits. (Methods of Markwood.)[8]

REAGENTS

(*a*) *Sodium hydroxide solution.* 0.5 per cent.

(*b*) *Calcium acetate solution.* Containing 4 g. of Ca per liter. May be made by warming 10 g. $CaCO_3$ with 12–13 g. of glacial acetic acid and diluting to 1 liter.

(*c*) *Acetic acid solutions.* A strong (about 30 per cent) solution, and a weaker solution (about 2 per cent).

(*d*) *Cyanogen bromide.* Prepared fresh before using by adding a fresh 10 per cent KCN solution dropwise to saturated bromine water until the latter is just decolorized. The solution is then diluted to 5 times its volume.

(*e*) *β-naphthylamine solution.* 0.2 g. dissolved in 100 ml. of 95 per cent alcohol. Prepare fresh and keep out of sunlight to avoid coloration; fresh solutions may exhibit moderate fluorescence in direct daylight.

(*f*) *Bentonite.* Powdered commercial grade.

(*g*) *Standard nicotine bentonite.* Prepared according to the method of Smith,[9] this is a convenient and fairly permanent standard. The nicotine is determined by the method on page 222, and ordinarily is from 5 to 8 per cent.

Standardization.

Treat 0.4 g. of nicotine bentonite with 400 ml. of the NaOH solution in a 1-liter volumetric flask and allow to stand a few minutes with occasional shaking. To this is added 400 ml. of distilled water, and then 20 ml. of the Ca acetate solution, with swirling. Make the solution to volume and mix well. After 15 minutes, by which time the flocculent precipitate has settled, the mixture is filtered rapidly through a fluted paper. To avoid disturbing the settled precipitate on decanting, the mixture is usually first transferred to a conical flask.

Pipette aliquots of the clear filtrate into 250-ml. volumetric flasks. These aliquots normally are 50, 100, 150, and 200 ml., and contain 20, 40, 60, and 80 ml., respectively, of the NaOH solution. To bring them to the same alkali content add 60, 40, 20, and 0 ml., respectively, of the NaOH solution. After the addition of 2 or 3 drops of phenolphthalein indicator, treat each solution with strong acetic acid almost to decolorization and then just decolorized, plus one drop over, with the weaker acid. The solution is then made to volume. A blank is also prepared but with ordinary bentonite replacing the nicotine bentonite. In this case a single aliquot of 200 ml. is taken.

Pipette a 5-ml. portion of each standard solution into a test tube, add exactly 1 ml. of the CNBr solution, and mix by swirling. Then add exactly 5 ml. of the naphthylamine solution, and mix well by further swirling. The tubes are stoppered and set aside in a dark cabinet for 1 hour, and read in a photometer or photoelectric colorimeter, using filter transmitting in the vicinity of 490 millimicrons.

Construct a graph showing the relationship between concentration and photometric reading. A straight line should be obtained for the range investigated, viz., 0–16 micrograms of nicotine per ml. This line passes through the blank as well as through the other points. A typical graph is shown in Figure 31.

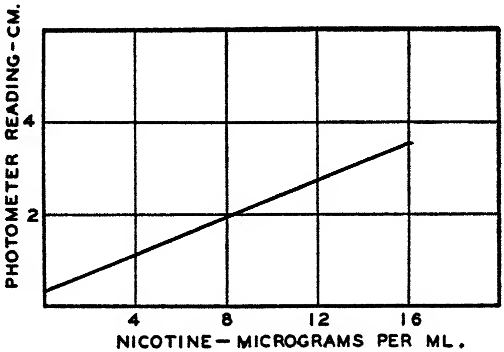

FIG. 31. Typical calibration curve for nicotine determination (method of Markwood).

Determination.

Place the sample of fruit in a suitable closed container and shake with the NaOH solution (reagent *a*). The container may be a tin can, a glass bottle, or a bell jar having a glass plate clamped over the open end, and should be provided with a draw-off valve. When the sample is large, a tin can is the most suitable container. Usually 10 mature apples are taken as a sample, 200 ml. of NaOH solution added, and the container shaken for 3 minutes. The liquid is drawn off into a 500-ml. volumetric flask, and the fruit shaken a minute or so again, first with 180 ml. and then with 80 ml. of water, and each washing drawn into the flask. About 0.2 g. powdered bentonite is then dispersed in this solution, followed by 10 ml. of the calcium acetate solution (reagent *b*), and the whole made to volume with water. Filter the mixture, withdraw a 200-ml. aliquot, and treat as described under "Standardization," beginning with "After the addition of 2 or 3 drops." From the curve obtained during the standardization, read off the amounts of nicotine present.

Oil Deposited on Apple Bark During Dormant Spraying. (Method of Pearce, Avens and Chapman.[10])

Sampling.

Cut 50 twigs at random from various parts of the tree or trees to be sampled. The twigs cut should average about 7.5 cm. (3 inches) in length, and about 0.5 cm. (3/8 inch) in diameter. Twigs having numerous buds and spurs or other highly irregular surfaces should be avoided as much as possible. Usually wood from the 2 or 3 year old growth is most suitable.

Extraction.

The twig sample is transferred to a large Soxhlet extraction apparatus and extracted for 1 hour with petroleum benzin (b.p. 35°–60° C.). A Soxhlet of the following size is necessary: inside diameter of extraction tube, 70 mm.; siphon tube, 165 mm. high; extraction flask, 1000-ml. capacity. The outfit is used without extraction thimbles. After extraction, the twigs are removed and the greater part of the petroleum benzin distilled off (it may be recovered by collection). The residue is transferred to a 125-ml. Squibb separatory funnel containing a plug of fat-free cotton in the stem so that the funnel acts as a filter to remove any particles of dirt or bark from the extract. The last trace of oil in the extraction flask is transferred to the separatory funnel by rinsing with petroleum benzin.

Transfer the contents of the separatory funnel, small amounts at a time, to a tared 125-ml. Pyrex Erlenmeyer flask containing two glass beads. Each portion transferred is carefully evaporated by placing the flask on an electric hot plate kept at low heat. In this manner the extract is freed from solvent. The separatory funnel is rinsed several times with petroleum benzin and the rinsings transferred and evaporated as indicated. The flask containing the oil residue is now heated for 1 hour at 100° C., cooled in a desiccator and weighed. Blanks are run on unsprayed samples of twigs in the same manner as above, and the weight of natural oil thus obtained subtracted from the weight of oil on the sprayed twigs: the difference is the amount of oil applied as spray. This may be calculated per unit of surface (bark) area of the twigs by measuring the total length of the twigs extracted and their volume by displacement; area in square inches then equals $0.55\sqrt{Vh}$, where V is the volume displaced in ml., and h the length in centimeters.

Phenothiazine. (Method of Cupples [11]).

Determination.

The phenothiazine residues to be determined are dissolved in 95 per cent ethyl alcohol, and an aliquot containing up to 4500 micrograms transferred to a 100 ml. volumetric flask. Enough alcohol is added to bring the volume to about 50 ml., and the flask and contents warmed to 60° C. Five ml. of saturated bromine water are added quickly to the alcoholic solution in the flask, the flask stoppered, and allowed to stand for 15 minutes in an oven at 60° C., and then a second 5 ml. of saturated bromine water quickly added. After the flask has stood for 10 minutes longer, the excess bromine is boiled off, the solution cooled, diluted to a definite volume, and filtered through a folded filter, the funnel being covered to minimize evaporation. After thorough mixing, the solution is measured in a photometer or photoelectric colorimeter, using a light filter transmitting in the region of 520 millimicrons. Standard curves are prepared in the usual way, using known amounts of phenothiazine, and the amount of phenothiazine in the unknown sample read from them, or the standards may be used for direct comparison in a visual colorimeter. The same method may be used, by regulation of the amount of original sample, to determine phenothiazine in commercial samples of the material.

Bromine Residues in Foods Fumigated with Methyl Bromide.

(Method of Shrader, Beshgetoor and Stenger [12]).

REAGENTS

Methylene chloride. Commercial material usually contains a trace of hydrolyzable bromide which may be removed by shaking 2 liters of the solvent with 15 grams of potassium hydroxide dissolved in 300 ml. of 95 per cent ethyl alcohol and allowing the mixture to stand for several days. The alcoholic potassium hydroxide is washed out with water and the methylene chloride is filtered, dried over anhydrous calcium sulfate, and distilled.

Alcoholic potassium hydroxide, 2.5 grams of potassium hydroxide per 100 ml. of 95 per cent ethyl alcohol.

Sodium hydroxide, analytical reagent grade.

Sodium peroxide, analytical reagent.

Hydrochloric acid, about 6 N. This should be as free from bromide as possible. C. P. acid may be diluted to 6 N and distilled, the first and last fractions (each about 10 per cent of the

total) being discarded to eliminate most of any free bromine or hydrobromic acid.

Procedure.

Total Bromide. A sample of 5 to 10 grams is treated in a 100-ml. nickel crucible with 40 ml. of alcoholic potassium hydroxide, allowed to stand for an hour, and evaporated to dryness on a steam bath. It is then dried for a short time at 110° C. and is covered with 10 grams of sodium hydroxide pellets. The crucible is kept for an hour or two on a hot plate until the bubbling or smoking diminishes, after which it is placed in a muffle at 600° C. Fusion should be carried out without excessive burning or foaming; if the charge becomes ignited, the crucible should be removed from the muffle until the flame is extinguished. It is then returned to the muffle and this process repeated until the volatile gases have been removed. Sodium peroxide is added to the melt, a few milligrams at a time, to complete the oxidation of the remaining carbon or organic matter. The peroxide must be added cautiously while the crucible is removed from the furnace; bromide is lost if the charge burns with a flare when too much peroxide is added.

Complete combustion of the organic matter can be effected best by returning any organic matter that has raised above the sodium hydroxide to the bottom of the crucible, where it mixes with the melt and is easily destroyed by addition of the peroxide. This is accomplished by carefully rotating the hot crucible to wash down the organic matter and adding 0.5 gram more of peroxide. If no burning or bubbling takes place, the oxidation is complete. A few carbon particles which may remain after the final addition of sodium peroxide do not affect the accuracy of the results.

The crucible is rotated to allow the melt to solidify on the sides, and cooled, and the contents are dissolved in 75 ml. of water. Solution of the sodium compounds is hastened by placing the crucible on a hot plate for several minutes. The solution is transferred to a 500-ml. beaker and partially neutralized with about 50 ml. of 6 N hydrochloric acid. The solution is boiled to destroy peroxides and to reduce the volume to 100 to 125 ml. Nickel hydroxide and other insoluble hydroxides are removed by filtering through a No. 2 Whatman paper, collecting the filtrate and washings in a 500-ml. wide-mouthed Erlenmeyer flask. The

filtrate is made slightly acid with 6 N hydrochloric acid, then neutralized with sodium hydroxide solution, adjusting to the color change of methyl red. The volume at this point should be approximately 150 ml.

About 2 grams of sodium acid phosphate and 5 ml. of hypochlorite solution (1 N NaClO in 0.1 N NaOH) are added and the mixture is heated to boiling. After a minute or so 5 ml. of sodium formate solution (50 grams per 100 ml.) are introduced and boiling is continued for 2 minutes. The sample is cooled and treated with a few drops of 1 per cent sodium molybdate solution, 0.5 gram of potassium iodide, and 25 ml. of 6 N sulfuric acid. Titration should be made immediately with standard 0.01 N sodium thiosulfate solution, starch indicator being added just before the end point. A blank on all the reagents should be carried through the entire procedure and subtracted. One milliliter of 0.01 N thiosulfate is equivalent to 0.1332 mg. of bromide ion.

Separation of Organic Bromide. A sample of 5 to 10 grams in a 100-ml. beaker is treated with 15 ml. of methylene chloride and filtered immediately on a Gooch crucible with a dry asbestos pad, rinsing with three 5-ml. portions of solvent. In filtering by suction, the sample should not be allowed to become so cold from evaporation that moisture condenses on it. Most of the sample is transferred back to the beaker without disturbing the asbestos pad and is allowed to stand for 5 minutes with 15 ml. of methylene chloride. If a sample is lumpy it should be ground with the solvent in a mortar at this stage, then filtered and rinsed as before. The solid is again returned to the beaker and treated with 15 ml. of methylene chloride, this time for a 15-minute period, followed by a third filtration and rinsing in the same crucible.

The filtrate, which is ordinarily discarded, contains most of any methyl bromide or other soluble organic bromide, but not all, since the extraction may have been incomplete and since volatile compounds may have escaped. The presence of a soluble bromide compound may, if desired, be detected by catching the filtrates in alcoholic potassium hydroxide and determining the inorganic bromide formed after evaporation to dryness and ashing. Whether or not the bromide so found is methyl bromide or a nonvolatile organic halide may be ascertained by making a duplicate set of extractions and evaporating the extracts to about half of their

original volume before addition of alcoholic alkali. Methyl bromide is expelled during this process and nonvolatile bromide may be determined on the remainder after hydrolysis and ashing. In this way the authors have found that within experimental error no organic bromide is formed by reaction of methyl bromide with the products that have so far been tested.

To remove any incompletely extracted volatile bromide compounds, the sample remaining after extraction is returned to the original beaker and treated with 15 ml. of methylene chloride. This is evaporated to dryness while being stirred to prevent bumping, but it should not be overheated. When the sample appears dry, the beaker is laid on its side in a warm place, such as on top of an oven, until all the odor of methylene chloride is gone.

Inorganic Bromide. Inorganic bromide may now be determined by the same procedure as described above for total bromide, practically all of the organic bromide having been removed. However, in order to have further confirmation of the inorganic nature of the remaining bromide, it has been shown in all the authors' tests to be water-soluble. The beaker and its contents are cooled, 30 ml. of water are added with thorough mixing, and then the mixture is filtered on the original crucible. In the case of some foods, such as flour, filtrations are very slow and preliminary separations by centrifuging are desirable. After each separation the solid is mixed with 30 ml. of water and allowed to stand for 15 minutes, then filtered or centrifuged again, until four extractions have been made. The combined filtrates are treated with 3 ml. of saturated sodium chloride solution and evaporated nearly to dryness in a silica dish, then 30 ml. of 2.5 per cent alcoholic potassium hydroxide are added and evaporated and the bromide is determined after ashing as described in the previous paper.[13]

Unaccounted Bromide. The residue after water-extraction may be placed in a 100-ml. nickel crucible and analyzed for bromide in the manner described under Total Bromide. Generally only a very small fraction of the total bromide will be found in this residue and the amount will be less the more thorough the water washing. Therefore this bromide is usually considered to be inorganic. Only in some experiments in which methyl bromide was adsorbed upon charcoal has the unaccounted bromide been thought to be

organic. No food adsorbs methyl bromide as tenaciously as does charcoal.

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